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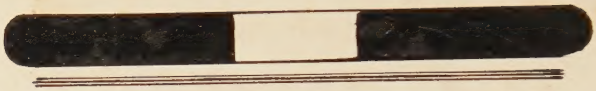

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THE COMPLETE SCHOOL CHEMISTRY

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PREFACE

It has been my endeavour, in compiling this course in theoretical and practical chemistry for schools, to make it complete in the sense that all that is usually taught in school should be contained in one volume. The book provides a general elementary course suitable for candidates for the London Matriculation, Army Entrance, Oxford Senior Local, and Cambridge Senior Local examinations. It will be found that the syllabuses of these examinations are covered by the following chapters :—

Matriculation—i.-xxiv., xxix.-xxxi., xxxiii., xxxv., xxxvi.-xxxix., xlii., xlvi.

Army Entrance—i.-xvi., xviii.-xxi., xxiii., xxiv., xxix., xxx., xxxv., xxxvi., xxxviii.-xl., xlii., xliii., xlvi.

Oxford Senior Local—i.-xxiv., xxix.-xliv., xlvi.

Cambridge Senior Local—i.-xxiv., xxx.-xxxiii., xxxvi., xxxviii., xxxix., xlii., xlv., xlvi.

Pupils find it difficult to read a book in which laboratory experiments are interspersed among the theoretical matter. This difficulty I have tried to overcome by collecting the experiments at the beginning of each chapter, and presenting the theoretical work in a continuous form in the remainder of the chapter. The experiments have been carefully chosen, and the theory is gradually and systematically built up. Equations and formulæ, avoided in Part I, are introduced in Part II, when the pupil is already so far familiar with the subject that he may use them with advantage.

I have purposely repeated in later chapters some of the

early work, and at the same time have amplified it in order to avoid back reference, to provide revision, and to widen the range of teaching from what was possible at an early stage to what has been rendered possible by subsequent study. This treatment will, I hope, make the book suitable as a continuous course for pupils moving rapidly up a large school.

The figures are diagrammatic throughout, and have been made as simple as possible, so that pupils will find no difficulty in reproducing them.

I desire to acknowledge my indebtedness to Mr. Fenton for his kind permission to make use of parts of his excellent "Notes on Qualitative Analysis" for the tables in the Appendix; to the University of London for permission to print Matriculation questions; to my colleagues Mr. F. W. Russell and Mr. L. Beesley for suggestions on physical and botanical points respectively; and to my colleague Mr. F. C. Boon for his kindness in reading the proofs.

F. M. OLDHAM

DULWICH, 1911

PREFACE TO THE TWENTY-FIRST EDITION

In this edition manufacturing processes have been brought up to date, new matter on the Ionic Theory has been introduced, and a new chapter on the Periodic Classification and on the Structure of the Atom has been added. Minor alterations have also been made in many places.

F. M. O.

Dulwich, 1923

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THE COMPLETE SCHOOL CHEMISTRY

PART I

CHAPTER I

SOLUBILITY—CRYSTALS—NATURAL WATERS

Experiment 1—To use a balance and weights

Make a careful drawing of the balance, letter each part of your drawing, and learn the names given to the different parts. Your figure should be in the form of a diagram, as in Fig. 1.

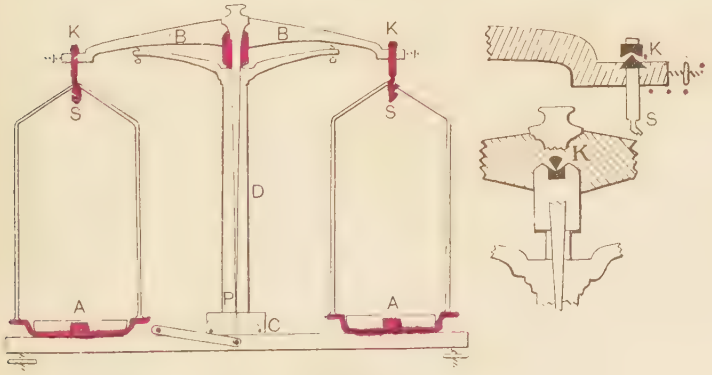


FIG. 1

B = Beam
K = Knife edge
P = Pointer
S = Stirrup
A = Scale pan
C = Scale
D = Pillar

Fig. 1 shows a simple form of balance. The beam **B** is supported on a steel or agate knife edge **K**, which rests on an agate plane or in a steel notch at the top of the pillar **D**. To

the centre of the beam is attached the pointer **P**, which moves in front of the scale **C**. Resting on steel or agate knife edges at the ends of the beam are the stirrups **SS**, on which are hung the pans **AA**. When the lever is turned to the right the knife edge **K** is supported solely by the agate plane, and the beam can swing. When the lever is turned to the left the knife edge no longer rests on the plane, and in most balances the scale pans touch the wooden base of the balance. The balance is always left in this position when not in use, so that the knife edges may not be worn away uselessly. The position is known as the *position of rest.*

Next note the positions and values of the weights. They are usually arranged as follows :—

50 grams	5 grams	0.5 gram	0.05 gram
20 grams	2 grams	0.2 gram	0.02 gram
20 grams	2 grams	0.2 gram	0.02 gram
10 grams	1 gram	0.1 gram	0.01 gram

The small weights are often marked in milligrams. Thus—0.5 grm. =500 mgms., 0.2 grm. =200 mgms., 0.1 grm. =100 mgms., 0.05 grm. =50 mgms., 0.02 grm. =20 mgms., 0.01 grm. =10 mgms.

The following rules must be observed :—

(1) Never put anything on the balance pans, or take anything off the pans, unless the balance is in the position of rest.

(2) Anything which may make the metal dirty or injure it must not be placed on the bare pan. Crystals, liquids, powders, etc , must be weighed on watch glasses or in glass vessels.

(3) Put the weights on the right hand pan with the forceps provided. **On no account touch the weights with your fingers.**

(4) When you begin to weigh, at first try a weight which you think will be too heavy ; remove it ; try the next smaller weight, and add other weights in the order in which they are placed in the box.

You will waste time if you do not choose the weights systematically.

(5) Write down the values of the weights before removing

them from the pan, and check your result as you put back the weights into their proper places in the box.

(6) Never weigh anything which is hotter or colder than the air.

If you have carefully read through these rules, you will be in a position to use a balance without injuring it.

Notice whether the pointer of your balance swings equally to each side of the central point of the scale. If it does not, screw outwards or inwards the little weight at the end of the beam until the pans are perfectly balanced.

Weigh a pencil, pocket-knife, watch, or any small object.

Exp. 2—To observe the properties of common substances

Required—Sand, chalk, wood, salt, sugar, water, glycerine, glass, copper, lead, etc.; test-tubes, pocket-knife

Directions—Examine very carefully each of the substances given to you. Notice the following points :—

(1) Whether the substance is a solid or a liquid.

(2) Colour.

(3) Smell.

(4) Hardness of substance. Test the hardness with your finger nail, and with a knife.

(5) If the substance is a liquid, notice whether it flows quickly or slowly.

(6) Whether the substance is soluble or insoluble in water. Put a very small quantity into a test-tube and shake with water. Does it seem to dissolve ?

(7) Heat a small quantity in a test-tube and note if it melts or boils readily.

Make a table of your results similar to that shown below.

Substance	State	Colour	Smell	Hardness	Power of flow	Solubility	Melts or boils
Silver	Solid	White metallic	None	Fairly hard	None	None	Does not melt
Turpentine	Liquid	Colourless	Strong	None	Flows easily	Insoluble	Boils readily

Exp. 3—To find out if a substance changes in weight when dissolved in water

Required—Balances, beakers, salt, sugar, glass rods, watch glasses.

Directions—Half fill the beaker with water, put in the glass rod, and cover the beaker with a watch glass, on which a few grams of salt have been placed. Weigh the whole. Next, carefully drop the salt into the water, stir until all is dissolved, and again weigh. Note your results.

Repeat the experiment, using sugar instead of salt.

Exp. 4—To find out if there is a limit to the amount of salt or other soluble substance which will dissolve in a given quantity of water

Required—Beakers, glass rods, saltpetre, Epsom salts, etc.

Directions—Put a small quantity of water into a beaker and add some saltpetre. Stir until all the saltpetre is dissolved. Add more saltpetre, stir again, and go on in the same way until you can be certain that there is or is not a time when no more saltpetre will dissolve.

Repeat the experiment with some other soluble substance.

Exp. 5—To see if more or less of a soluble substance is dissolved by hot water than is dissolved by cold water

Required—Substances used in Exp. 4

Directions—As before, add saltpetre to a small quantity of water in a beaker until no more is dissolved. Now place the beaker and its contents on a tripod stand covered with wire gauze, and warm gently with a small bunsen flame. Add from time to time small quantities of saltpetre, and stir. Is more dissolved by hot or by cold water?

Repeat the experiment with other soluble substances.

Exp. 6—To find out whether writing chalk is soluble or insoluble

Required—Powdered writing chalk, small flasks or beakers, filter funnel, evaporating dish

Directions—Half fill a small flask with distilled water, put in a pinch of powdered chalk, and boil over the wire gauze

for a few minutes. Can you see any difference in the amount of writing chalk present ?

Now fold a filter paper (your hands should be dry) in the manner shown in Fig. 2. Fit the folded paper into the funnel, moisten it with water, and filter the mixture of chalk and water into an evaporating dish. *A filter paper should never be filled more than two-thirds full.*

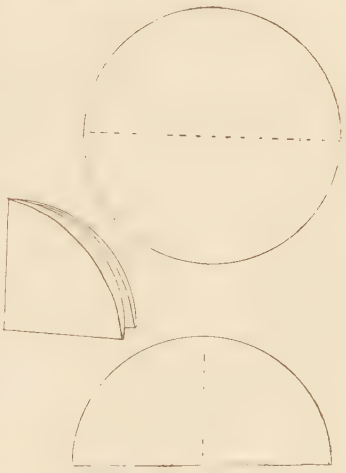


FIG. 2

Boil down the clear liquid, or *filtrate,* which runs through the paper until no water remains. Anything left behind in the dish must have been dissolved in the water. Perhaps the small quantity of solid left in the dish was contained in the water before the writing-chalk was put in. Find out if this is the case by boiling down in a clean evaporating dish as much distilled water as you used of the filtrate.

You should now be able to say whether writing chalk is soluble or insoluble in water.

Exp. 7—To find the solubility of a substance at a given temperature, and to plot a curve of solubility

Required—Flask, water bath, thermometer,* 10 *c.c. pipette, evaporating dish, saltpetre, potassium chlorate, or other salts*

Directions—Put about 50 c.c. of distilled water into a small flask, and place the flask in a water bath heated by a small flame, Fig. 3. Add to the water in the flask more of the salt provided than will dissolve at the temperature at which you are working.

Gently stir the contents of the flask with the thermometer. Keep the temperature inside the flask as nearly constant as

* Golden syrup tins, paint tins, etc., with a hole cut in the lid, make efficient water baths.

you can for ten minutes by regulating the heating of the water bath and by stirring with the thermometer. Next draw off with the pipette 10 c.c. of the clear liquid in the flask, and put it into a weighed evaporating dish. Weigh again. Evaporate to dryness on the water bath. Dry and re-weigh the dish. Put down your results as follows :—

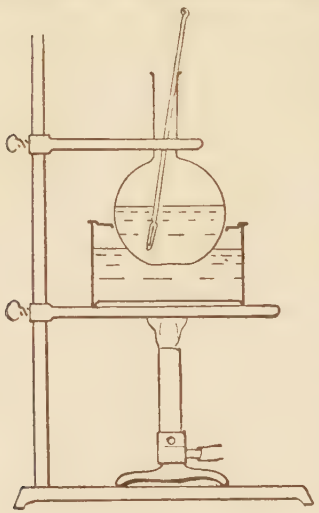


FIG. 3

Weight of dish and 10 c.c. of solution at t° C. . . =
Weight of dish . =_____
Weight of 10 c.c. of solution . . =_____
Weight of dish and solid . . =
Weight of dish . =_____
Weight of solid =_____

You can now calculate the weight of solid dissolved by 100 grams of water at t° C. Convenient values for t° C. are 20°, 30°, 40°, 50°, etc.

Alternative Method—Tie a piece of cotton round the top of a clean dry test-tube, and suspend the test-tube by a loop in the cotton from the stirrup of a balance. Weigh the tube. Into it put about three grams of finely powdered potassium chlorate. Weigh again. Add about 5 c.c. of distilled water and weigh again.

Next put a thermometer into the water, and warm very gently above a bunsen flame, stirring all the time with the thermometer. Read the temperature when the last trace of potassium chlorate disappears. Allow the solution of potassium chlorate to cool, still stirring with the thermometer, and read the temperature when the first crystals of potassium chlorate appear. Repeat the warming and cooling at least twice, each time taking the temperature when the crystals disappear and appear. The mean of the six or more readings will give you fairly accurately the temperature at which the potassium chlorate saturates the water you have taken. You know the weight of the chlorate and the weight of the water, and you can easily calculate the weight of chlorate dissolved by 100 grams of water.

The solubility of the chlorate at a second temperature can be obtained by the addition of a measured quantity of distilled water from a burette or graduated pipette. One c.c. of distilled water weighs 1 gram.

If the results obtained by others of your class have been written on the black-board, you can draw a curve showing the solubility of the salt at various temperatures. Mark on

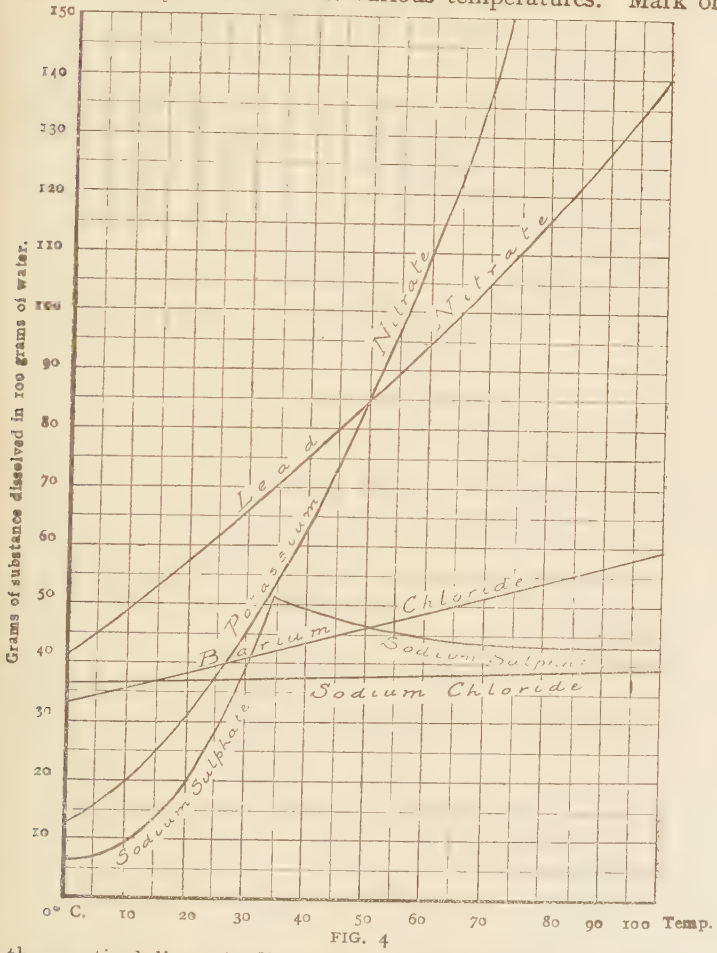


FIG. 4

the vertical lines (ordinates) the number of grams of solid dissolved by 100 grams of water, and mark the temperatures on the horizontal lines (abscissæ). The curves in Fig. 4

show the solubility of lead nitrate, sodium sulphate, barium chloride, etc., at temperatures from 0° C. to 100° C.

Exp. 8—To find out if common substances, soluble or insoluble in water, are soluble or insoluble in other common liquids

Required—Methylated spirit, turpentine, paraffin oil, vinegar, salt, sugar, paraffin wax, chalk (limestone), sand, test-tubes

Directions—Put a very small quantity of each solid in turn into a test-tube, add one-third of a test-tubeful of liquid, and gently warm. With methylated spirit and turpentine, take great care that the liquid, or vapour from the liquid, does not come near the flame. Note whether the solid dissolves, and put down your results in tabular form.

If you are not quite sure whether a solid is soluble in a liquid, you can make certain by evaporating to dryness on a watch glass a few drops of the clear liquid standing above the solid in the test-tube. Use a very small flame, and place the watch glass about six inches above it. A residue on the watch glass indicates that the substance is soluble.

Exp. 9—To obtain specimens of saltpetre, sulphur, and charcoal from a mixture of the three substances

Required—Mixture, filter, beakers, evaporating dishes, carbon bisulphide, water bath

Directions—Saltpetre is soluble in water, but insoluble in carbon bisulphide. Sulphur is soluble in carbon bisulphide, but insoluble in water. Charcoal is insoluble in both water and carbon bisulphide.

Boil a few grams of the mixture with 30 to 50 c.c. of water in a beaker. Filter. Evaporate the solution to a small bulk and allow to stand.

Wash the residue on the paper at least three times with a small quantity of hot water, to remove the rest of the saltpetre, *each time allowing the water to drain through completely before adding more water.* Why? Dry the paper and its contents in the steam oven.

Next remove the residue of sulphur and charcoal to a beaker, and shake these substances with carbon bisulphide. Filter; wash several times with warm carbon bisulphide to remove the rest of the sulphur.

Evaporate the solution of sulphur on the water bath in a

draught chamber until crystallisation begins. Dry the charcoal in the steam oven, or by pressure between blotting paper.

The solution of saltpetre should now be cold. Is there any saltpetre to be seen? If not, boil down further, and again cool. Dry the saltpetre crystals with blotting paper.

Exp. 10—To find the percentage of insoluble matter in a mixture of a soluble and an insoluble substance

Required—Filter, beaker, balance, wash bottle, mixture

Directions—Weigh a filter paper. Weigh a beaker, and into it weigh about 5 grams of the mixture. Add about 50 c.c. of water to the mixture, and warm. Grease the lip of the beaker in the way shown by the shading in Figs. 5 and 6. Why is this done?

Pour the clear liquid down a glass rod into the filter in the manner shown in Fig. 5. Now warm up the mixture remaining in the beaker with about 20 c.c. of water, and again pour the liquid into the filter Do this at least three times. Finally, wash out the solid from the beaker into the filter, using a jet of water from your wash bottle for the purpose. Dry the paper and insoluble matter in the steam oven, and weigh. Calculate the weight of insoluble matter in 100 grams of the mixture.

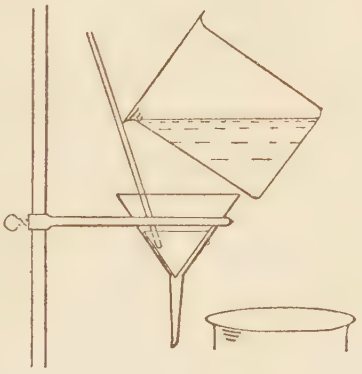


FIG. 5 FIG. 6

Alternative Method—Weigh a filter paper, fold it, and into the folded paper put about 3 grams of the mixture. Weigh again. Place the paper in a filter funnel, wash the mixture 10 or 12 times with small quantities of hot water, dry the paper and insoluble matter, and weigh again. Calculate the percentage of insoluble matter in the mixture.

Exp. 11—To prepare crystals of soluble substances

Required—Powdered alum, lead chloride, copper sulphate, washing soda, salt, etc.

Directions—With each of the substances provided make a

hot saturated solution in about half a test-tubeful of water; filter if the solution is not clear, and allow to cool. Draw and compare the various crystals you obtain.

If you have time, make a saturated solution of one or two of the substances from which you have obtained crystals, and try the effect of cooling the outside of the tube by means of running water. What effect has rapid cooling on the shape and size of the crystals?

Keep your specimens for the next experiment.

Exp. 12—To observe the effect of heating crystals

Required—Small test-tubes, crystals from Exp. 11, *sal ammoniac and iodine*

Directions—Thoroughly dry with blotting paper the crystals obtained in Exp. 11. Heat in a small test-tube a few crystals of each kind. What happens? Do all the crystals behave in the same way?

Now heat iodine and sal ammoniac separately, and compare the results with those previously obtained.

Exp. 13—To find out if the liquid which is given off when some crystals are heated is water

Required—Copper sulphate, washing soda, small test-tubes, glass rod, retort and flask, turpentine, oil, evaporating dish

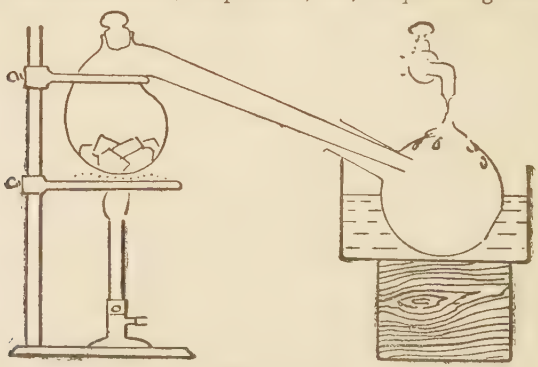


FIG. 7

Directions—Heat a small quantity of copper sulphate in a test-tube until it is white. Add a drop of water from a glass

rod to the white solid, and notice the change of colour. Try if the same change of colour is brought about by a drop of turpentine or oil. You have now a means of telling if a liquid is water, for only those liquids which contain water will cause the colour change you have noticed.

Fill a small retort with crystals of washing soda and connect it to a well-cooled flask, Fig. 7.

Heat the retort until no more liquid drips into the receiver. Put a drop of the liquid on heated copper sulphate. Taste the liquid, evaporate some of it to dryness in a dish and note whether there is a residue, and finally find apparatus shown in Fig. 8.

A large test-tube may be used instead of the flask in Fig. 8.

The boiling point of water is 100° C.

Next examine the residue left in the flask. Is it crystalline? What happens when water is added to it? Dissolve some of it in water and try to obtain once more crystals of washing soda.

Similar experiments may be tried with other crystalline substances which give off water on heating.

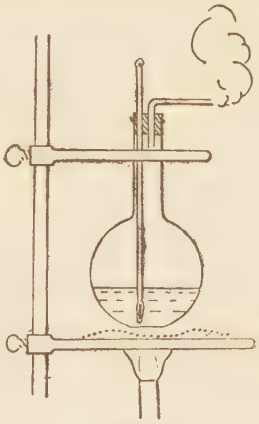


FIG. 8

Exp. 14—To find the percentage of water contained in some crystals

Required—Crucible and lid, triangle, balance, copper sulphate, barium chloride, Epsom salts, etc.

Directions—Clean, dry by warming, and weigh the crucible and lid. Weigh into it between 1 and 2 grams of the powdered salt given to you. Arrange your apparatus in the manner shown in Fig. 9.

Gradually increase the size of the flame as the water is driven off, but do not make the bottom of the crucible red hot. Why not? After heating for about ten minutes, allow the crucible to cool. Re-weigh.

Again heat fairly strongly, but not to redness, for five minutes. Cool; re-weigh. Repeat the heating and weighing until two consecutive weighings are the same.

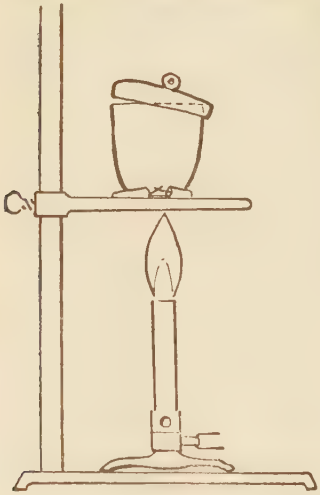


FIG. 9

Calculate the percentage of water in the salt given to you.

When you boiled various solutions, or evaporated them on the water bath, you sent water into the air. All the solid in the solution remained behind. If, then, the water sent into the air is recovered, it should be very pure.

Exp. 15—To obtain pure water from a solution

Required—Salt solution, retort, flask cooled by water, evaporating dish

Directions—Fit up a clean retort and flask as in Fig. 10.

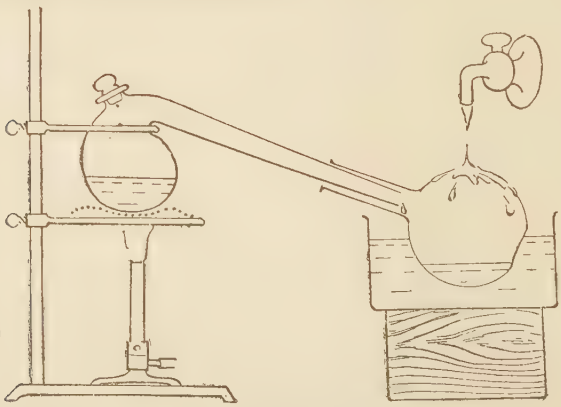


FIG. 10

Half fill the retort with salt solution and heat gently over wire gauze. When you have obtained about 50 c.c. of liquid

in the flask, stop the experiment. Taste the liquid in the flask, evaporate about 10 c.c. to dryness in an evaporating dish over wire gauze, and find the boiling point of the rest. Is the liquid pure water?

Exp. 16—To find the amounts of dissolved solid in rain water, tap water, river water, sea water

Required—20 c.c. pipette, evaporating dish, water bath, balance

Directions—Weigh a clean, dry, evaporating dish, and into it put 20 c.c. of the water given to you. Evaporate to dryness on the water bath, and weigh again. Notice how your result differs from those of boys who have been supplied with different water.

Exp. 17—To find the effect of natural waters on the lather-producing power of soap

Required—Small pieces of soap, evaporating dishes, natural waters, 20 c.c. pipette

Directions—Put 20 c.c. of the given water in an evaporating dish. Rub the soap under the water with the tips of your fingers until there is a lather on the surface of the water. Note the time you have taken to obtain the lather.

Now, wash and dry the basin, and repeat with 20 c.c. of another water. Note the time taken to produce as much lather as before. Repeat, using other waters. Do you notice any relation between the amounts of solid matter (Exp. 16), dissolved in various waters, and the time taken to produce a lather?

Solids and liquids

Some liquids, such as water or ether, flow quickly, and are therefore said to be *mobile*. Other liquids, such as glycerine or treacle, flow slowly, and are said to be *viscous*. Pitch flows so slowly that most people would call it a solid. A lump of pitch, however, when placed on a flat surface gradually becomes flat. If a thin cake of pitch is put on three or four upright pegs, and on the pitch are placed several leaden bullets, in the course of a few months the pegs make their way upwards through the pitch and the bullets fall through. If pitch were a true solid, this would not happen.

A true solid does not flow, and it keeps its shape even when unsupported at the sides. A liquid requires support at the sides, and it takes the shape of the vessel containing it.

Solubility, Saturation, etc.

Some substances dissolve easily in water; others dissolve only slightly; others apparently do not dissolve at all. Examples of the first class are salt, saltpetre, Epsom salts. Writing chalk or plaster of Paris is an example of a slightly soluble substance. Sand, copper, limestone, and glass are insoluble substances. Even such substances as sand, limestone, and glass are very slightly soluble, but their solubility is so small that it may be neglected in all our experiments.

There is a limit to the solubility of any solid substance. Water will dissolve more than its own weight of sugar, but it will not, even when hot, dissolve twenty times its weight of sugar. Almost all solids are more soluble in hot than in cold water. It is for this reason that, when a solution is wanted quickly, the mixture of solid and liquid is warmed. A considerable time would be required to make a strong solution of alum in cold water, but the solution can quickly be obtained by heating the water.

At a particular temperature the amount of a solid which can be dissolved by a particular weight of water is always the same. When water at any definite temperature has dissolved as much as it can of a solid, the solution obtained is said to be a **saturated solution** at that temperature.

It is often necessary to state exactly the solubility of a substance at a particular temperature. The amount dissolved in 100 grams of water is usually stated.

We can say, therefore, that *the* **solubility** *of a substance at a particular temperature is the number of grams of the substance which dissolve in* 100 *grams of water at that temperature.*

Fig. 4 shows the solubility from 0° C. to 100° C. of various salts. The solubility of sodium sulphate increases regularly to 34° C., and then gradually diminishes. The solubility curve for lead nitrate is much steeper than those for common salt and barium chloride, while the curve for saltpetre becomes steeper and steeper as the temperature rises. It would seem, therefore, that if you had a solution of equal parts of common salt and saltpetre, you could get crystals of salt by boiling

down the solution. Owing to the small solubility of salt and the great solubility of saltpetre at high temperatures, the water would be saturated with salt long before it was saturated with saltpetre. The salt would therefore crystallise.

Could you separate common salt from barium chloride in the same way?

Such curves as those shown in the figure are very useful, for they show at a glance the solubility of a salt at any temperature between 0° C. and 100° C.

Crystallisation, Sublimation, etc.

You have found out that, when a hot saturated solution of a soluble substance is allowed to cool, crystals of the substance separate. Some substances seem to take up water as they crystallise, others do not. Washing soda crystals contain much water, common salt crystals contain none. The water taken up in this way by crystals is called **water of crystallisation**.

The results obtained by the class will show that crystals of one substance contain a fixed proportion of water, but that different substances contain varying percentages of water. You may imagine that each minute particle of a substance possesses the power of attaching to itself a definite number of particles of water. Thus, each particle of Epsom salts attaches to itself seven particles of water, each particle of washing soda ten particles of water, and each particle of alum twenty-four particles of water. Common salt, however, takes up no water when it crystallises. Chemists give to the minute particles the name of molecules.

You may wonder whether one substance always contains the same amount of water. If you find the percentage of water in freshly made washing soda crystals, and in crystals of washing soda which have stood in the open air for a week, you will discover that much of the water has disappeared from the exposed crystals. Put a crystal of washing soda into your waistcoat pocket and notice what happens to it.

Substances which give off the whole or part of their water of crystallisation on exposure to air are called **efflorescent** substances.

Other substances, such as calcium chloride, sodium nitrate, and caustic soda, instead of giving up water to the air, take

up from the air enough water to dissolve them. Such substances are called **deliquescent** substances.

You noticed on heating iodine and sal ammoniac that no water was given off, but that the substance itself seemed to be turned into vapour. This vapour, cooled down by the upper part of the tube, once more became solid, and gave crystals similar to those with which you started. Solid substances which do this are said to **sublime**, and the solid obtained in the cool part of the tube is called a **sublimate**.

Distillation

In Exp. 15 you obtained pure water from salt water by converting the water into steam and cooling down the steam in a separate vessel.

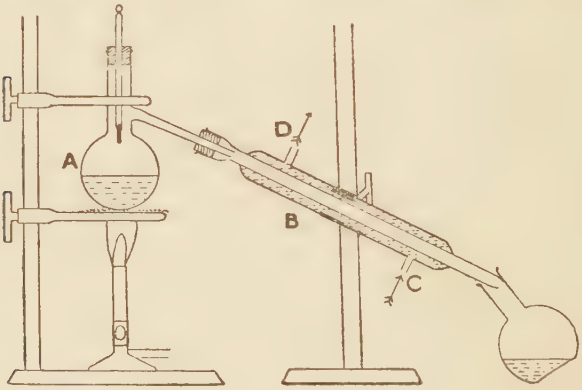


FIG. 11

The process of converting a liquid into vapour and condensing the vapour in a different vessel is known as **distillation**. A good apparatus for carrying out this process is shown in Fig. 11. The distilling flask **A** is fitted with a thermometer, the bulb of which comes about an inch below the side tube. If the liquid boils at a temperature below 70° or 80° C., the flask is heated on the water bath. If the liquid boils at a higher temperature, a sand bath or wire gauze must be used.

The cork used is made of ordinary cork. India-rubber corks can only be used for liquids which do not attack india-rubber, and do not boil at a temperature at which india-rubber

is melted. **B** is a *condenser*, consisting of an inner glass tube through which the vapour of the liquid passes, and of a wider tube of glass or metal which surrounds the inner tube. Through the outer tube or jacket, as it is often called, flows a stream of cold water. The lower tube **C** is connected to a water tap, and the upper tube **D** to a sink.

If the liquid boils at a high temperature, the condenser can be replaced by a wide glass tube. The air will cool this tube sufficiently. Aniline (boils at 180° C.) and nitrobenzene (boils at 207° C.) can be distilled in this manner. Distillation is most useful to the chemist, for it enables him to purify liquids from solid and liquid impurities.

NATURAL WATERS

Enormous quantities of water are converted into vapour by the heat of the sun. From all seas, rivers, lakes, ponds, etc., water is constantly being evaporated, but the evaporation in cold and temperate regions is small compared with that which takes place in the warm seas near the equator. From these warm seas great masses of water vapour rise with ascending currents of heated air, and flow north and south towards the poles. As the vapour is cooled on its journey towards the poles, much of it is condensed to water, and dropped on the surface of the earth as rain, snow, or hail. Rain ought, therefore, to be as pure as distilled water. It remains, however, in contact with the air for some time, and dissolves a small quantity of it. It also collects in its fall particles of dust, etc., which are floating about in the air. Consequently rain water is not pure water.

Part of the rain disappears into the ground, and part flows off the surface of the ground and forms streams, rivers, and lakes. The part which enters the ground may make its appearance again as springs, or it may be taken up by plants and trees.

A perfectly satisfactory classification of natural waters cannot be made. For convenience, they are divided below into four classes, viz. (1) rain water, (2) river and lake water, (3) spring water, and (4) sea water.

(1) **Rain water**—Rain which falls in country districts some distance from towns is the purest form of natural water. It contains some dissolved air and some dust. Otherwise it

is very pure. The rain which falls in towns, and in the neighbourhood of towns, is often very impure. It contains much dirt from coal smoke, and a small quantity of sulphuric acid derived from the sulphur in the coal. Ammonia and nitric acid may also be present. All rain water contains dissolved carbon dioxide.

(2) **River and lake water**—The water in the streams in granite and slate districts is frequently, owing to the insolubility of granite and slate, almost as pure as country rain water. The streams in limestone, chalk, and gypsum districts contain much chalk and gypsum in solution.

The Scotch and Welsh streams and rivers flow chiefly over insoluble rocks. They contain little dissolved matter. Loch Katrine, which supplies Glasgow with water, contains only 0.27 parts of dissolved solid in 10,000 parts of water.

The streams and rivers in Derbyshire and the South of England flow through districts containing much limestone. They therefore contain much more dissolved matter than the Scotch rivers. The Thames in the lower part of its course contains over 4 parts of dissolved solid in 10,000 parts of water. It has been calculated that the limestone, carried down to the sea in a year by the Thames, would make oyster shells sufficient to cover a square mile of ground to the depth of a foot. The Trent flows through a district containing much gypsum, and its water contains a considerable quantity of this substance. The water used at Burton-on-Trent is supposed to be particularly good for brewing on account of the gypsum it contains.

All rivers also contain some salt. Rivers flowing past large towns are contaminated with sewage and manufacturing refuse. The air dissolved by the water has a purifying effect on the refuse ; so that a river water, quite unfit for drinking purposes, may after flowing for many miles become once more fit to drink, owing to the action of the air and of other purifying agencies.

The water used by towns for their water supply is usually collected from uncultivated districts at some distance from towns. Water from cultivated land might contain harmful impurities derived from manure and decaying vegetable matter.

(3) **Spring water**—Fig. 12 illustrates the way in which springs are frequently formed. The figure represents a

vertical section through a hill. **A** is a mass of gravel, sandstone, chalk, or other material, which will allow water to percolate into it. **B** is a bed of clay or impervious material, which will not allow water to pass through it. The rain falling on **A** penetrates the pervious rock and trickles downward until it reaches **B**. It cannot pass through **B**, and consequently it flows along the top of **B** until it bursts out at **C** as a spring. A second spring may in very wet weather be formed at **D**. Such places as Winterburn probably derive their names from the existence of springs which flow only in the wet winter months.

FIG. 12

It is obvious that the water remains in contact with **A** sufficiently long to dissolve some of the rock. The more soluble the rock **A**, the more of it will the water dissolve. The rocks, with which the spring water may come into contact, may vary considerably in composition. Spring water may therefore be expected to contain impurities, which vary in character and amount, in proportion as the water has been in contact with soluble or insoluble rocks for a long or short time. Some springs contain hardly any dissolved matter; others contain so much that the water has a decided taste. The latter are known as *mineral springs*. There are brine springs in Cheshire, borax springs in Tuscany, and other mineral springs in Harrogate, Cheltenham, Tunbridge Wells, Carlsbad, Marienbad, etc. Mineral springs may contain common salt, borax, Epsom salts, Glauber's salts, salts of iron, sulphuretted hydrogen, and small quantities of many other substances. Mineral waters containing iron are known as *chalybeate* waters. Seltzer water, Apollinaris water, and Perrier are spring waters, which contain much carbonic acid gas. They effervesce naturally as they flow from the ground

(4) **Sea water**—The solid matter, carried down by rivers in solution to the sea, is not converted into vapour by the sun's heat. It must, therefore, be increasing in quantity. The following table (Thorpe and Morton) shows the amounts of substances present in 1000 parts of sea water taken from the Irish Channel :—

	Weight of solid in 1000 parts of water		Weight of solid in 1000 parts of water
Common salt	26.44	Magnesium nitrate	trace
Magnesium chloride	3.15	Lithium chloride	trace
Magnesium sulphate	2.07	Ammonium chloride	trace
Calcium sulphate	1.33	Iron carbonate	trace
Potassium chloride	0.75	Silica	trace
Magnesium bromide	0.07		
Calcium carbonate	0.05	Total	33.86
Magnesium carbonate	trace		

Although rivers do not contain much salt, the sea contains a greater proportion of salt than of other substances. This is probably because rivers long ago removed most of the easily soluble salt from their drainage areas. The small amount of limestone present in sea water is accounted for by the small solubility of calcium carbonate, and by the fact that the greater part of the hard parts of sea animals consists of calcium carbonate. This substance, when the animals die, is deposited on the bottom of the sea as limestone or chalk, and covered up by the sand and mud brought down by rivers before the water has completely dissolved it. The huge masses of limestone in England and in other countries have almost without exception been formed in the sea.

Salt lakes, such as the Dead Sea and the Salt Lake of Utah, may contain five or six times as much solid matter as the Irish Channel.

CHAPTER II

ELEMENTARY STUDY OF AIR

Exp. 18—To find the effect of heat on various substances in presence and absence of air

Required—Wires of platinum, iron, copper, magnesium ; pieces of lead, zinc, tin, sulphur, and charcoal ; iron spoons, hard glass ignition tubes, crucible tongs, emery paper

Directions—If they are not already clean, rub the pieces of wire with emery paper until they are bright.

Heat the wires separately in the bunsen flame for a short time, holding them in crucible tongs. Notice what happens in each case. Remove the wire from the flame, allow it to cool, and notice any change in its appearance. If possible, again rub the wires with emery paper, and see if the change is only on the surface or goes all through the metal. Next heat separately the pieces of lead, zinc, tin, sulphur, and charcoal in iron spoons, and observe any change. If a tarnish forms on the molten metal, scrape it to one side with a knife, and go on heating the metal and removing the tarnish for some minutes. In all the experiments air has been able to get at the heated substance freely.

If the substances are heated in small tubes, very little air can get at them. Try the effect of heating each substance in an ignition tube.

Tabulate your results as follows :—

Name of substance	Description of substance	Effect of heating in the flame or on a spoon	Is the effect only on the surface, or throughout the substance ?	Effect of heating the substance in a tube
Iron	White metal, hard and bright	Iron becomes white hot in the flame, and a black tarnish is formed	The tarnish is only on the surface	The iron is only slightly tarnished

What conclusions can you draw from these experiments as to the effect of the presence or absence of air on the substances heated ?

Exp. 19—To see whether there is a change of weight when some of the substances used in Exp. 18 are heated in air

Required—Platinum wire, copper filings, iron filings, zinc, tin, sulphur, magnesium ribbon, phosphorus, crucible lids or small porcelain dishes, balances, triangles

Directions—Weigh a small quantity of one of the substances into a porcelain dish. Heat for some minutes on a triangle over a bunsen flame, allow to cool, and weigh again. See Fig. 13. In the case of magnesium it is better to use a crucible and lid, in order that the white fumes may not escape.

The air should be admitted occasionally by raising the lid slightly with the crucible tongs.

Note any alteration in weight.

Could the escape of the fumes from the sulphur be prevented in the same way?

Exp. 20—To find out if the fumes from burning phosphorus weigh more than the phosphorus

Required—Calcium chloride tube fitted with cork and tubing; glass wool, aspirator, balance, phosphorus

Directions—Put a piece of phosphorus, about the size of a pea, into the bulb of the calcium chloride tube. Next, push into the tube a plug of damp, but not wet, glass wool; put in the cork and tube; and weigh the tube and its contents.

Fit up the rest of the apparatus as shown in Fig. 14.

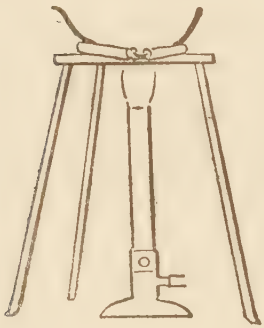


FIG. 13

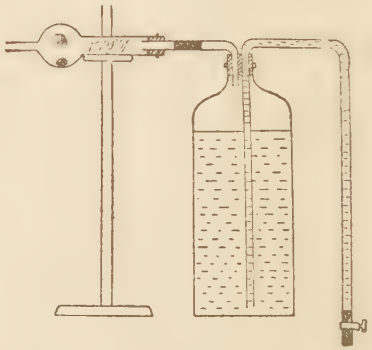


FIG. 14

Allow water to run from the aspirator, and, if the phosphorus does not light spontaneously, warm it gently until it does. Regulate the stream of water flowing from the aspirator until practically no fumes escape from the calcium chloride tube. Allow to cool. Re-weigh.

Are the fumes from burning phosphorus heavier than the phosphorus?

Exp. 21—To find out if air is altered by the burning of phosphorus in it

Required—Wide-mouthed bottles, pneumatic troughs or soup plates, small evaporating dishes, pieces of phosphorus, glass plates

Directions—Float an evaporating dish, containing a small piece of phosphorus, on water in a pneumatic trough ; light the phosphorus by touching it with a hot glass rod, and carefully place over it a wide-mouthed bottle. See Fig. 15. Notice all that happens. Is the height of the water in the bottle, before and after the experiment, the same ? When all the white fumes from the phosphorus have dissolved in

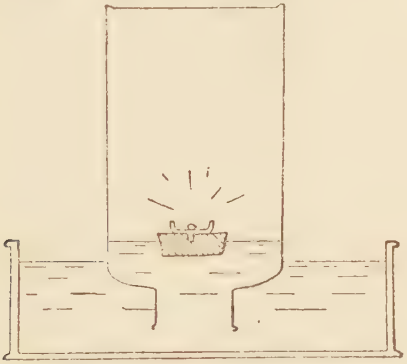


FIG. 15

the water, put a glass plate under the bottle, and place the bottle right way up with the plate still covering it. Now put a lighted splinter in the air left in the bottle. Is the residual gas the same as ordinary air ?

Next measure the water in the bottle ; then completely fill the bottle with water and again measure it. The volume of the water sucked up will give you the volume of the air used up by the phosphorus, and the volume of the water filling the bottle will give the volume of the air you started with. What is the proportion of air used up in the burning of phosphorus ? Repeat the experiment once or twice, and take the mean of your results.

Before leaving the laboratory set up the apparatus for Exps. 22 and 23.

Exp. 22—To find the proportion of air used up in the rusting of iron

Required—Gas jars or wide-mouthed bottles, pneumatic troughs or soup plates, iron filings, measuring cylinder

Directions—Sprinkle the inside of the bottle with water and scatter iron filings on the sides and bottom. Invert the bottle in water. Allow to stand for a few days. Note the change in the iron filings. Test the residual gas with a lighted splinter. Measure (1) the water sucked up, and (2) the volume of the bottle.

Is the proportion of air used up by iron in rusting the same as the proportion used up by the phosphorus in the last experiment?

Note.—The bottle may be replaced by a test-tube, which can be inverted in a beaker or gas jar half full of water.

FIG. 16

Exp. 23—To find the proportion of air taken up by cold phosphorus

Required—Measuring tube, phosphorus fixed on a thick wire, gas jars or bottles

Directions—Partly fill the measuring-tube with water, and invert it in a large pneumatic trough or corked-up sink. Note carefully the volume of the air in the tube when the water inside is level with the water outside the tube. Why must the level be the same inside and outside? Introduce a piece of phosphorus on a wire into the tube, bend the wire up at the bottom, and place the whole in a wide-mouthed bottle or gas jar. See Fig. 16. Remove the apparatus from the trough, put it by for a few days, and if possible note the level of the water from day to day. When the water has ceased to rise, once more level in a large deep vessel filled with water, remove the phosphorus, and read the volume of the air remaining in the tube. Invert the tube on your thumb, and test the residual air with a lighted splinter. The part of the air which is used up by the phosphorus or iron is called *oxygen*.

Exp. 24—To find the weight of a litre of air

Required—Round-bottomed flask of about 500 c.c. capacity, fitted with india-rubber cork carrying a short piece of glass tubing, to which is attached a short piece of india-rubber tubing compressed by a clip ; balances, measuring cylinder

Directions—See that your apparatus is fitted up in the manner shown in Fig. 17.

Into the flask put about 100 c.c. of water, take off the clip, and boil the water for at least ten minutes in order to expel the air in the flask. Next, remove the flame, and quickly put on the clip while the water is still boiling. Cool the flask with cold water, dry the outside, and weigh it.

Open the clip, and weigh again. The increase in weight is the weight of the air that has entered.

Find the volume of the air by measuring (1) the water left in the flask, and (2) the volume of water which fills the flask to the level of the cork.

Calculate the weight of 1000 c.c. of air.

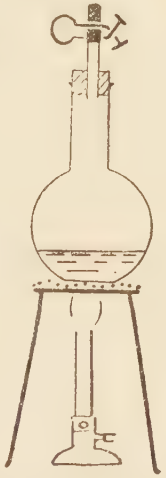


FIG. 17

Note—More accurate results can be obtained if corrections are made for the effect of the temperature and pressure of the air at the time of the experiment. See Boyle's Law and Charles' Law.

Exp. 25—To make oxygen from the calx or oxide of mercury, and from other substances

Required—Mercuric oxide, ferric oxide, potassium chlorate, manganese dioxide, red lead, copper oxide, oxygen splinters, ignition tubes

Directions—Heat a small quantity of each of the substances in an ignition tube. From time to time hold a glowing splinter inside the top of the tube.

From which substance do you get oxygen most readily ?

Now mix three parts of powdered potassium chlorate with one part of manganese dioxide, and heat the mixture.

Does the mixture give better or worse results than the single substances?

Exp. 26—To prepare oxygen and examine its properties

Required—Small flasks, potassium chlorate, manganese dioxide, pneumatic troughs, gas jars, deflagrating spoon, splinters, sulphur, phosphorus, magnesium, charcoal, sodium, iron wire, litmus solution, lime-water

Directions—Fit up an apparatus like that shown in Fig. 18. Bend the glass tube by holding it across the width of a bats-wing flame. Gently rotate the tube as it softens, and bend slowly to the required shape. In the small flask place

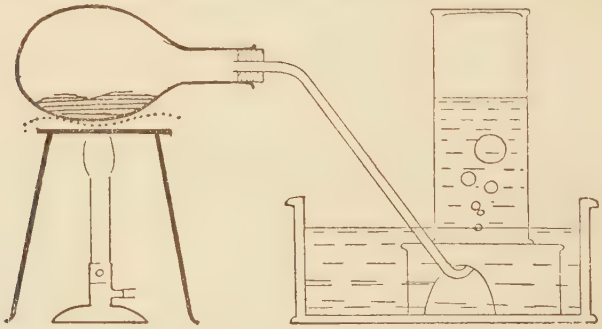


FIG. 18

20 to 30 grams of a mixture of three parts of potassium chlorate (fine powder) and one part of manganese dioxide, and heat gently. Fill several gas jars with water, invert them in the trough, and displace the water from them by passing in oxygen. Take out the jars, as soon as they are full of gas, by means of ground glass plates, and leave the plate on the top of each jar so that the oxygen may not escape. When you have filled all the jars you possess, remove the flame from the flask and take the glass delivery tube out of the water, so that the water may not be sucked back into the flask as the latter cools.

Test the oxygen in the jars as follows :—

Jar I. Invert in water, and notice whether oxygen dissolves.

Jar II. Put a glowing splinter into the jar.

Jar III. Put in glowing charcoal on a deflagrating spoon. Afterwards pour in a few c.c. of purple litmus solution, cover with a glass plate, and shake. Is the colour of the litmus changed?

Jar IV. Repeat the experiment with charcoal. Add a few c.c. of lime-water, and shake. What happens?

Jar V. Introduce burning sulphur on a deflagrating spoon. Afterwards add purple litmus, as with Jar III.

Jar VI. Dry a piece of phosphorus (as large as a pea) with filter paper, put it in a deflagrating spoon, light it, and introduce it into Jar VI. Test the product with litmus. **On no account touch the phosphorus with your fingers.**

Jar VII. Burn a piece of magnesium ribbon in this jar. Shake up the product with purple litmus solution.

Jar VIII. Dry a piece of sodium (the size of a pea) with filter paper, heat it in a deflagrating spoon until it begins to burn, and quickly introduce it into the jar. Shake up the product with purple litmus solution. **Do not let the sodium come into contact with any water, and do not touch it with wet hands.**

Jar IX. Make a piece of thin iron wire white hot and plunge it quickly into the oxygen. Test the product with purple litmus solution.

Note down systematically the results you have obtained.

Exp. 27—To find the weight of oxygen given off when 100 grams of potassium chlorate are heated, and to examine the residue

Required—Potassium chlorate, crucible and lid, triangle, balance, dilute nitric acid solution, silver nitrate solution, test-tubes

Directions—Weigh a clean dry crucible and lid (a hard glass test-tube may be used in place of a crucible). Into the crucible weigh about 1 gram of powdered potassium chlorate. Put the covered crucible on a triangle, and gently heat for a minute or two. Gradually increase the temperature until the bottom of the crucible is red hot. Allow to cool. Weigh.

Again heat to redness for about five minutes. Cool and weigh again. Repeat this heating and weighing until two successive weights of the crucible and its contents are the same. This is the only good method of telling when all the oxygen has been driven off.

Calculate the percentage weight of oxygen driven off.

The percentage of oxygen from mercuric oxide can be found in a similar way, by heating a weighed amount of the oxide in a hard glass tube which is at least six inches long.

Fill with distilled water the crucible containing the residue from the potassium chlorate, and gently warm on the wire gauze. Pour the clear solution into a test-tube. Now make a solution of a few crystals of potassium chlorate in distilled water. To each of the solutions you have obtained add a few drops of dilute nitric acid, and some silver nitrate solution. Do the solutions give the same results? What do you conclude?

EFFECTS OF HEAT ON SUBSTANCES

From very ancient times it was known that some metals, such as gold and silver, were not affected by heating in air. Metals, not spoilt by fire, were called *noble metals*. It was also known that iron, copper, and lead were changed on long heating in the air, either wholly or partly, into a dross. These metals were called *base metals*. The substance produced by heating a metal strongly in air was called a *calx*.

Various suggestions were made to account for the burning of bodies, and for the conversion of metals into calxes. The most important was put forward by Stahl, a German chemist, at the close of the seventeenth century. This suggestion, called the *Phlogistic Theory*, was made use of by chemists for about a hundred years. Stahl and his followers thought that all bodies, which could burn or be converted into a calx, contained a substance, which they named Phlogiston (Greek, *φλογίζειν = to set on fire*). The burning was said to be due to the escape of phlogiston into the air. A metal was said to lose phlogiston when converted into a calx.

Eventually, it was noticed that a metal became heavier when it was converted into a calx. To account for this, some of the believers in the phlogistic theory said that phlogiston was the "principle of lightness," and that when phlogiston escaped the substance losing it became heavier. Others, however, began to think that the phlogistic theory was wrong.

Exps. 18 and 19 seem to show that air has something to do with the change of a metal into a calx. Later experiments proved this.

LAVOISIER'S EXPERIMENTS

Exps. 21, 22, and 23 clearly show that something is taken out of the air when phosphorus burns, iron rusts, or yellow phosphorus is allowed to stand in air. Other substances burnt in air give the same results. One-fifth of the air is used up, and the air left behind will no longer allow substances to burn in it. What has become of the used-up air? The phosphorus when burnt gave white fumes quite different from phosphorus. The iron became coated with a red rust. Can the used-up air have become joined on to the phosphorus and iron?

Lavoisier, a very clever French chemist, who was guillotined

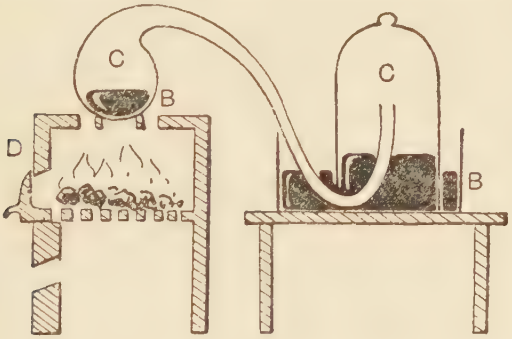


FIG. 19

B=Mercury **C**=Air **D**=Furnace

in the French Revolution, set himself in 1772 to answer this question. Instead of using phosphorus or iron he used tin. He proved, by heating tin in air in a suitable vessel, that the air lost in weight exactly as much as the tin gained in weight. It was obvious, therefore, that the lost air was fixed in the tin.

The next thing he had to do, was to find out the nature of the air used up. In 1774 an English chemist, Priestley, had found out that when he heated the calx of mercury he got a gas, which allowed things to burn in it more brightly than in air. He told Lavoisier about his discovery. This knowledge led Lavoisier to carry out the following experiment, which has since become famous. The apparatus he used is shown in Fig. 19.

In the bulb he put clean, dry mercury. The bulb was connected by a bent tube to the air in the bell jar. He heated the retort for twelve days to a temperature near the boiling-point of mercury. Red specks formed on the surface of the mercury, but they did not increase in quantity after the twelfth day. The volume of air in the bell jar diminished. The fire was put out, the red calx was collected, and the air in the bell jar was measured. He then heated the calx, and got from it Priestley's gas, which allowed substances to burn in it, and animals to breathe in it, better than ordinary air. The volume of the gas obtained he found to be exactly equal to the volume of the air used up. The residual air would not allow substances to burn in it, or animals to live in it.

When the gas, obtained from the calx of mercury, and the residual air were mixed together once more, ordinary air was obtained. He had, therefore, fixed part of the air in the mercury, and got back again this part by heating the red substance produced. He thus proved that, when mercury was turned into a calx, there was no need to suppose that phlogiston was given out, but that a portion of the air, which had weight, was fixed in the mercury. This experiment practically dealt the death-blow to the Phlogistic Theory. The experiment clearly shows that the part of the air, which is used up in breathing and burning, is the same as the gas obtained by heating the calx of mercury. This gas Lavoisier named **oxygen** (Greek, *'οξύς = sour*, *γεννάω = I produce*). The gas remaining after oxygen was taken out of the air he called *azote* (Greek, *α, privative*, *ζωή = life*). This gas is now called **nitrogen** (Greek, *νίτρον = saltpetre*, *γεννάω = I produce*).

PROPERTIES OF OXYGEN

Your experiments have taught you many of the properties of oxygen. These properties are collected below :—

Oxygen is a colourless gas, without smell or taste. It is almost insoluble in water. It will not burn. It will relight a glowing splinter. Carbon, sulphur, and phosphorus burn in it more brightly than in air, giving substances which turn purple litmus solution red. The metals magnesium and sodium burn in oxygen more readily than in air, giving substances which turn purple litmus blue. Iron wire, which burns with difficulty in air, burns brightly in oxygen, giving

a black solid which is insoluble, and which has no effect on litmus.

The substances produced by the burning of the metals, etc., in oxygen are called **oxides.** The oxides of the metals either turn litmus blue or have no effect on it. Such oxides are called **basic oxides.** Sodium oxide, magnesium oxide, and iron oxide are basic oxides. The calxes of the metals, therefore, are basic oxides, not metals from which phlogiston has escaped. Simple bodies, which are not metals, *i.e.* the non-metals, burn in oxygen, giving substances which turn litmus red. These oxides are called **acidic oxides.** Carbon dioxide, sulphur dioxide, and phosphorus pentoxide, which were produced by the burning of carbon, sulphur, and phosphorus in oxygen, are acidic oxides.

PROPERTIES OF NITROGEN

You should have learned from your experience of nitrogen, the gas left when oxygen was taken from the air, that it is a colourless gas, without smell or taste. It is less soluble than oxygen. It will not burn or allow substances to burn in it. You are always breathing air, so that it is clear that neither oxygen nor nitrogen is poisonous.

In air, therefore, there are two different substances, oxygen and nitrogen in the proportions one of oxygen to four of nitrogen. Whether these gases are joined together in any way, or are simply mixed, you have yet to learn. Your experiments have not proved that these are the only substances present in air. In fact, you know well that another substance must be present in air, viz. water, which frequently falls as rain. In the next chapter you will try to find out whether water is a simple substance or is made up of different substances.

PRACTICAL EXERCISES

(1) Find out if the following substances are soluble or insoluble in water: (*a*) barium sulphate, (*b*) lead chloride, (*c*) iron oxide, (*d*) red lead, (*e*) manganese dioxide.

(2) Find the solubility of potassium chloride at 15° C., 40° C., 65° C., and 90° C.

(3) You are given a mixture of chalk, sand, and salt. Try to obtain a pure dry specimen of each substance.

(4) Find the percentage of saltpetre present in gunpowder.

(5) Find the percentage of salt in the given mixture of salt and sal-ammoniac.

(6) Find the percentage of water present in the mineral gypsum.

(7) From powdered ferrous sulphate and powdered alum prepare crystals of the two substances.

(8) Find out whether one-fifth of the air is used up when a candle burns.

(9) Find the weight of a litre of oxygen. 1 litre of air weighs 1.293 grams.

Note.—The oxygen should be washed from particles of potassium salts, carried over by the gas, by passing it through water contained in a small flask.

(10) Find the percentage weight of oxygen given off when mercuric oxide is heated.

(11) Find the volume of oxygen given off when 1 gram of potassium chlorate is strongly heated.

CHAPTER III

ELEMENTARY CHEMICAL STUDY OF WATER—ELEMENTS, COMPOUNDS, AND MIXTURES

Exp. 28—To observe the action of metallic sodium with water

Required—Small pieces of sodium, pieces of narrow leaden tubing closed at one end, pneumatic troughs, evaporating dishes, gas jar, litmus

Directions—Throw a small piece of sodium on to water contained in an evaporating dish. What happens? Try to light the gas which comes off from the sodium. When all the sodium has disappeared, add a few drops of purple litmus to some of the water from the dish. Evaporate down the rest of the water in the dish. Describe the residue. What happens when it is exposed to air for some time?

You will remember that, when sodium was burnt in oxygen, the sodium oxide produced turned purple litmus blue. Can it be that the sodium has taken oxygen from the water and set free this gas which burns? You will find out later if the other metals, magnesium and iron, behave in the same way.

Now put a piece of sodium in the leaden tube and hammer the open end of the tube until a hole not much larger than a pin head is left. **Caution**—*The experiment is dangerous unless the hole left is very small.* Place the tube under a gas jar filled with water and inverted in a pneumatic trough. When the gas no longer comes off, remove the jar with a glass plate and test the gas with a lighted splinter. What happens?

Exp. 29—To find out if magnesium and iron will split up water

Required—Hard glass tube drawn out at one end, flask, connecting tubes, pneumatic trough, gas jars, magnesium ribbon, iron filings, litmus, asbestos

Directions—Put small pieces of iron and magnesium into water. Does either metal act on water like sodium? Perhaps there is no action because the water is cold. Try heating the water. Next try the effect of steam on the strongly heated metal.

Fit up a flask, hard glass tube, and collecting apparatus in the manner shown in Fig. 20. The hard glass tube should be slightly inclined upward, so that condensed water may not flow on to the hot glass and crack it.

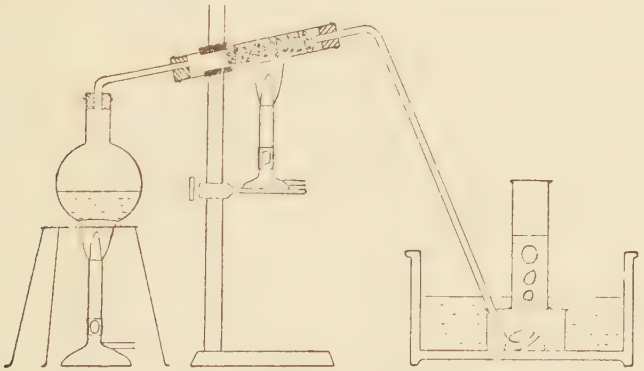


FIG. 20

Into the flask put about 100 c.c. of water, and into the hard glass tube about ten grams of iron filings. Keep the filings in the middle of the tube with loose plugs of asbestos. Drive a current of steam through the apparatus to remove the air. Why? Put the gas jar in position and heat the iron, at first gently and then strongly. When the jar is full of gas, stop the boiling of the water, and disconnect the hard glass tube. Why? Test the gas in the jar with a lighted taper. Does it behave in the same way as the gas from sodium and water?

Examine the metal in the tube. What do you think has happened to it?

Repeat the experiment, using magnesium ribbon instead of iron. Notice if the white residue resembles magnesium oxide,

and try if it has the same effect as magnesium oxide on purple litmus solution.

Exp. 30—To try to obtain from acids the inflammable gas which is contained in water

Required—Hydrochloric acid, nitric acid, sulphuric acid ; iron, magnesium, zinc, copper, lead, tin ; test-tubes

Directions—Hydrochloric acid, nitric acid, and sulphuric acid, when heated, have characteristic smells. First heat a few drops of each acid and note the smell.

Put a small piece of one of the metals into a test-tube and cover it with about a sixth of a test-tube of hydrochloric acid. Note the smell and colour of any gas evolved, whether the gas burns or allows a splinter to burn in it, and whether the metal dissolves entirely or leaves a residue.

Now dilute some hydrochloric acid with three or four times its volume of water and repeat the experiment with the metal.

Repeat with the other metals and acids, using both strong and dilute acid. First try cold acid ; afterwards heat.

N.B.—To make dilute sulphuric acid, pour the acid into water in a thin stream and stir thoroughly. [Do not pour the water into the acid.]

Tabulate your results as follows :—

Metal	Hydrochloric Acid	Sulphuric Acid	Nitric Acid
X	Readily soluble in both dilute and strong acid, giving a colourless, odourless gas, which burned but did not allow a taper to burn in it. No residue.	Dilute acid had hardly any action. Cold strong acid had no action. With hot strong acid it gave a colourless gas with an irritating smell, like that of burning sulphur. The gas would not burn or allow things to burn in it. No residue.	No action.

With hydrochloric acid you will have found that a number of metals gave a inflammable, odourless gas, like the gas you have already obtained in Exps. 28 and 29.

Dilute sulphuric acid with some metals gives the same gas,

but hot strong sulphuric acid usually gives a gas smelling like burning sulphur. You have probably got no inflammable gas when you used nitric acid. Instead, a reddish-brown gas with a sharp smell has been obtained.

What metal and what acid would you use if you wanted to obtain a quantity of the inflammable gas?

Exp. 31—To prepare hydrogen, the inflammable gas obtained in Exps. 28, 29, and 30, and to examine its properties

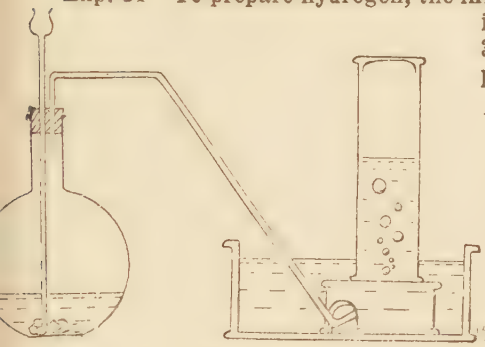


FIG. 21

Required—Flask, thistle funnel, delivery tube, trough, jars, zinc, dilute hydrochloric acid, cork bored with two holes

Directions—Fit up the apparatus shown in Fig. 21. Into the flask put granulated zinc and pour the acid down the funnel.

Carry out the following experiments with the gas obtained:—

Jar I. Put in a lighted taper.

Jar II. Repeat. Is there any difference? What is the cause of the difference?

Jar III. Invert the jar, remove the plate, and put a lighted taper well into the jar. Does the taper burn in the gas?

Jar IV. Take off the plate and allow the jar to stand for a minute or two. Put in a lighted taper. Explain the result.

Jar V. Try to pour upwards the hydrogen from this jar into a somewhat smaller and well-dried jar filled with air. Apply a light to both jars.

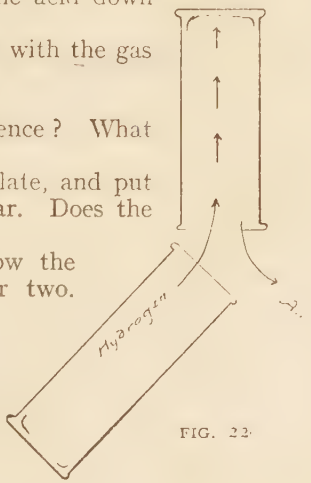


FIG. 22

What happens in each case? What can the mistiness in the upper jar be due to?

Could hydrogen be collected by passing the gas upwards into a jar?

Exp. 32—To examine the liquor obtained in the preparation of hydrogen

Required—Evaporating dish, filter paper, funnel, test-tube

Directions—Filter the liquid left in the flask in Exp. 31, and boil it down slowly in an evaporating basin on wire gauze or a sand bath. From time to time remove a few drops from the dish to a test-tube, and cool down the test-tube with water. If no crystals appear, put back the liquid and boil again. If you can get no crystals, evaporate to dryness. Examine the crystals or solid mass which you obtain.

Substances like this, obtained by dissolving a metal in an acid, are known as **Salts.**

Exp. 33—To find the volume of hydrogen obtained when one gram of a metal is dissolved in acid

Required—Zinc, magnesium, iron, sulphuric and hydrochloric acids; flask, short test-tube, cotton, gas jar and trough, measuring cylinders

Directions—The weights of metals used should be: for zinc and iron, not more than .5 gram.; for magnesium and aluminium, about .2 gram.

Tie a piece of cotton round the top of a short test-tube, and into the tube put an accurately weighed, clean piece of the metal. Fit a small conical flask with an india-rubber cork bored with one hole. If an india-rubber cork is not available, use a very sound ordinary cork. Into the flask put dilute hydrochloric acid. Fit up the apparatus in the manner shown in Fig. 23. For collecting the gas, a jar or bottle of

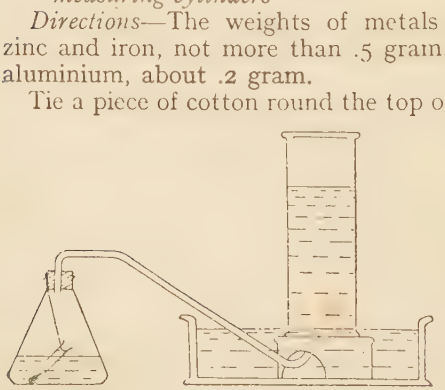


FIG. 23

about 300 c.c. capacity should be used. When all is ready, incline the flask until the acid comes into contact with the metal. From time to time change the acid in the tube by gentle shaking. Repeat until all the metal has dissolved. When all the gas has come off, put a greased ground-glass plate under the jar, press tightly so that no water can escape, and remove the jar. Now measure the water left in the jar; find how much water the jar can hold by filling it from a measuring cylinder. The difference gives you the volume of hydrogen obtained.

Alternative Method—In place of the test-tube and cotton, weigh the metal. Wrap it in a filter paper and drop into the acid, quickly replacing the cork in the flask.

Calculate the volume of hydrogen that would be obtained from one gram of the metal. Compare this volume with those obtained by others of your class with different metals.

The results of the class should show that the same volume of gas is always obtained from one gram of a given metal, but that different volumes are given by one gram of different metals.

Exp. 34 —To examine the moisture produced when hydrogen is burned

Required—Hydrogen apparatus, calcium chloride tube, retort, connecting tubes, test-tube

Directions—Fit up the apparatus shown in Fig. 24. The

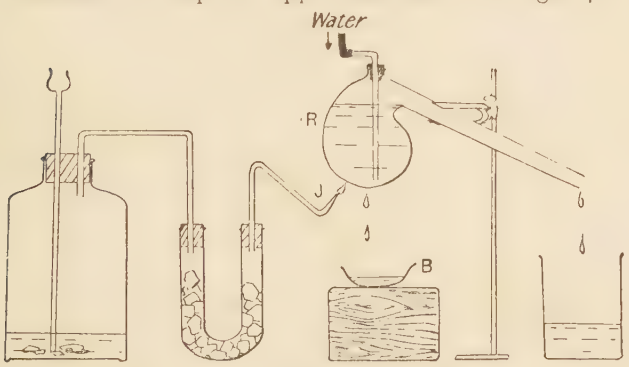


FIG. 24

U tube contains calcium chloride to dry the hydrogen evolved.

When hydrogen has been coming off for a minute or two, fill a test-tube with it by upward displacement, and apply a light to the mouth of the test-tube. If the gas burns quietly, the jet **J** may be lighted; if the gas makes a pop, do not light the jet, but test again until the gas burns quietly. Then light the jet. Explain these precautions.

Cold water flows through the retort **R**, and the moisture produced by the burning of the hydrogen collects in the basin **B**. The waste water from the retort runs directly into a sink or a large vessel.

Test the liquid as follows:—

(1) Taste it; (2) smell it; (3) evaporate a little to dryness on a watch glass, and see if there is a residue; (4) test it with white copper sulphate; (5) if you have enough of it, find its boiling point. What is the liquid?

Exp. 35—To separate a mixture of iron filings and sulphur, and to observe the effect of heat on the mixture

Required—Mixture of very fine iron filings and sulphur, magnet, carbon bisulphide, dilute sulphuric acid, funnels, filter paper, test-tubes

Directions—

(1) Shake a few grams of the mixture with water in a test-tube and try to separate the light sulphur from the heavy iron. Pour the water containing the sulphur in suspension into a filter. Repeat with more water.

(2) Try to separate the iron from another portion by stirring the mixture with the end of a magnet and blowing away the sulphur from the attracted mass.

(3) Shake in a test-tube a very small quantity of the mixture with about one-sixth of a test-tube of carbon bisulphide. Pour the clear liquid on to a watch glass. What is left in the tube? What appears on the watch glass as the carbon bisulphide evaporates?

Caution—*Carbon bisulphide is very inflammable.*

(4) To another small portion add dilute sulphuric acid. What happens to the iron and sulphur?

(5) Now take one-third of a test-tubeful of the mixture and heat it strongly. Why does the mass glow? Allow it to cool; break the tube, and examine the mass formed. Does it look either like iron or sulphur?

(6) Grind up the mass into a fine powder in a mortar and with portions of it repeat (1), (2), (3), and (4).

Write down in two parallel columns the results obtained with the mixture before and after heating. Try to account for the difference in the behaviour of the mixture before and after heating.

Exp. 36—To try to find out if air is a mixture or a compound

Required—Measuring tube, trough, 500 c.c. flask with cork and delivery tube, phosphorus on wire, water through which air has been blown or which has stood in air

Directions—Fit up the apparatus shown in Fig. 25, taking care that the end of the glass tube is level with the bottom of the cork. Fill the flask and tube completely with the water provided, boil out the dissolved air, and collect it in a measuring tube. Allow the tube to cool and then read the level of the gas in it. This gives you the volume of the boiled-out air. Next introduce a piece of yellow phosphorus on a wire into the tube. Either allow it to stand for a day in the trough, or, if more convenient, remove the tube to a jar by means of a crucible or small dish in the manner shown in Fig. 26. After the tube has stood for one or two days, remove the phosphorus and again read the level of the gas in the tube. The contraction caused by the phosphorus gives the volume of the oxygen present in the boiled-out air. Is the proportion of oxygen in the boiled-out air the same as in ordinary air?

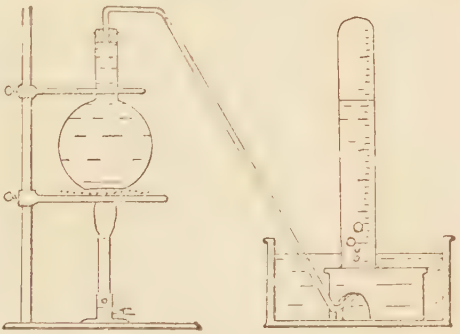


FIG. 25

In *compounds* the constituents are fastened together, *i.e.* combined together. In *mixtures* the constituents are not

fastened together chemically. If the nitrogen and oxygen in air are combined together, mere solution in water ought not to alter the proportion of oxygen to nitrogen. If the nitrogen and oxygen are not combined together, each gas will dissolve separately. Now, oxygen is twice as soluble as nitrogen. Therefore, if air is a mixture, the boiled-out air will contain more oxygen than ordinary air.

FIG. 26

This experiment does not prove absolutely that air is a mixture or a compound, because a compound of nitrogen and oxygen might be broken up into its constituents by close contact with water.

HYDROGEN AND WATER

You have found out that hydrogen is contained in water and in acids, and that it can be obtained from them by means of certain metals. When the metals decomposed water, they seemed to be converted to oxides. It appears probable, therefore, that oxygen is present in water. This is shown more clearly by the burning of hydrogen. When hydrogen burns in air, it unites with the oxygen of the air and gives a liquid which has all the properties of water. There is a possibility, however, that the hydrogen combines, not with the oxygen, but with the nitrogen of the air. All your experience has been against this possibility, and your experience teaches you correctly; for hydrogen burns in pure oxygen, producing water, and it cannot be made to burn in nitrogen. Nitrogen, therefore, can have nothing to do with the production of water when hydrogen is burnt in air. The name hydrogen means water-producer, from the Greek (ὕδωρ = water, γεννάω = I produce).

Let us now find out if possible the quantities of hydrogen and oxygen which unite to form water. Fig. 27 represents a vessel in which is placed water and two thin pieces of platinum, fastened to the end of wires from a battery. No change appears to take place. When a few drops of sulphuric acid are put into the water, bubbles of gas rise from both pieces

of platinum. Tubes filled with water are now placed over the platinum, and the gases are collected.

It will be noticed that the gas collecting at the positive plate, or **anode**, has exactly half the volume of the gas collecting at the negative pole, or **kathode**. When the gases in **A** and **K** are tested, it is found that a glowing chip introduced into the gas in **A** is relighted, and that the gas in **K** burns with a colourless flame. From the anode, therefore, comes one volume of oxygen, and from the kathode come two volumes of hydrogen. But, it may be suggested, if the gases only come off when sulphuric acid is added to the water, is it not likely that it is from the sulphuric acid that they are derived? No, it is from the water, because, however long the electric current is passed, the amount of sulphuric acid in the vessel remains unchanged, whereas the quantity of water diminishes.

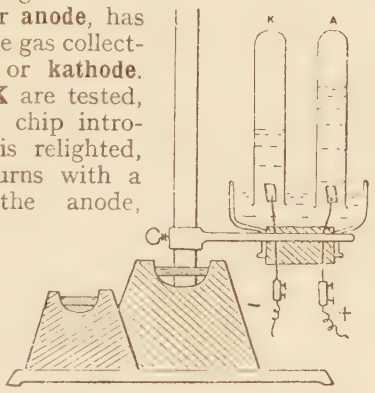


FIG. 27

It appears likely, therefore, that water consists of two volumes of hydrogen united with one volume of oxygen. If the platinum electrodes in the apparatus shown in Fig. 27 are placed close together, but not touching, the gases can be collected together. They should be collected in a strong tube. When a light is applied to the mixture, a violent explosion occurs, and the tube is made misty. If it can be proved that the mixture of two volumes of hydrogen and one volume of oxygen, when exploded together, give water, we can be certain that water consists of these gases combined in this proportion.

CAVENDISH'S EXPERIMENT

In 1781, Cavendish, an English chemist, carried out a number of experiments on the combination of hydrogen and oxygen. He used a glass globe furnished with a stop-cock and means of firing by electricity. This globe he exhausted with an air-pump, and then filled with hydrogen and oxygen

mixed in the proportion of two to one. The stop-cock was then shut and the mixture fired by electricity. More mixture was then admitted to the globe and exploded. By repeating the operation he obtained a liquid which possessed all the properties of water. No other product was obtained. He thus proved conclusively that water consists of hydrogen and oxygen, combined in the ratio of two volumes of hydrogen to one volume of oxygen.

You may have wondered if anything would have happened if three volumes of hydrogen and one volume of oxygen, or two volumes of oxygen and one volume of hydrogen, had been used in Cavendish's experiment. Cavendish and other chemists have tried various volumes, and have found that, if other volumes than two of hydrogen and one of oxygen are used, there is always either oxygen or hydrogen left over after the explosion. For example, if 40 c.c. of hydrogen are exploded with 10 c.c. of oxygen, 20 c.c. of hydrogen are left and no oxygen. If 30 c.c. of oxygen and 30 c.c. of hydrogen are used, 15 c.c. of oxygen are left and no hydrogen.

ELEMENTS, COMPOUNDS, AND MIXTURES

The remarkable difference that the spark or the lighted splinter makes to the mixture of hydrogen and oxygen must have been noticed. Before the light is applied, there are two gases, invisible, colourless, and without smell. Afterwards, there is a liquid, water, that can be produced, tasted, evaporated, boiled, and frozen. What can cause the difference? In the mixture of gases the oxygen and hydrogen, although mixed together, still keep their own properties. In the water all the properties of the oxygen and hydrogen have disappeared. A new substance with completely different properties has been produced. The hydrogen and oxygen can be mixed together in any proportion, but in water they are present only in a fixed proportion. All attempts to split up hydrogen and oxygen into simpler substances have failed.

Substances which up to the present time have not been split up into simpler substances are called **elements.**

When two or more elements combine together to form a substance with completely different properties, the substance formed is called a **chemical compound.**

A compound can be split up into simpler substances; and

the compound which you have studied, viz. water, can only have its constituents present in a fixed proportion.

A *mixture* may have its constituents present in any proportion.

Mixtures of substances can generally be separated into their constituents by mechanical means. Solution in various solvents, distillation, separation by taking advantage of differences of density, attraction by a magnet, etc., are mechanical means. Compounds cannot be separated into their constituents by mechanical means.

You were able to separate by mechanical means the iron and sulphur in Exp. 35 before heating. After heating, mechanical means would not separate the iron and sulphur. The heat had caused them to combine and form a chemical compound. This compound, iron sulphide, has properties quite different from those of iron and sulphur. It gives with acids an offensive-smelling gas ; it is not affected by a magnet, and no part of it is soluble in carbon bisulphide.

Exp. 36 shows that air which has been boiled out from solution in water contains much more oxygen than is contained in ordinary air. If air were a compound of nitrogen and oxygen, the boiled-out air would have the same composition as ordinary air. Probably, therefore, air is a mixture. The composition of air varies slightly in different parts of the world ; but a compound has a fixed composition. Therefore air is a mixture.

PHYSICAL AND CHEMICAL CHANGE

Several substances you have dealt with have been changed considerably, *e.g.* water to steam, cold platinum to white hot platinum which gives out light and heat, salt to a colourless solution, mercuric oxide to mercury and oxygen, metals with water to oxides and hydrogen, metals with acids to salts and gases, and finally a mixture of hydrogen and oxygen to water. If you think about these changes, you will conclude that they belong to different classes. Water, when changed to steam, was still water in a gaseous state and could easily be changed back to water by cooling ; platinum wire, heated to whiteness in a bunsen flame, although it gave out light and heat, was still platinum ; salt dissolved in water was still salt and could easily be obtained again by evaporating off the water. When

however, mercuric oxide was heated, metallic mercury and gaseous oxygen were formed, substances very different from the red powder from which they were obtained ; sodium with water gave a white solid different from sodium and hydrogen ; metals treated with acids gave gases, and, if the solutions were evaporated, salts which are substances different from the acids and metals used.

The first class of change is called *physical change* ; the second class *chemical change.*

Physical change *may be defined as a temporary change in the properties of a substance without any alteration in the actual material of which it is composed.* **Chemical change** *is a change in the material of the substance, other substances with properties different from those of the original substances being formed.* In other words, chemical change is a change in the composition of a substance.

INDESTRUCTIBILITY OF MATTER

The question now naturally arises as to whether, when chemical change takes place, matter is destroyed or created. In other words, do the substances produced weigh the same as the substances from which they are made ? The following experiments may help to provide an answer to this question.

A dry piece of phosphorus is dropped on to dry sand placed at the bottom of a round-bottomed flask. The flask is then tightly corked with an india-rubber stopper and weighed. It is next clamped to a stand, and placed in a draught chamber so that no damage will be done if it bursts during the experiment. The flask is gently warmed until the phosphorus lights, when the flame is taken away. The phosphorus burns until the oxygen is exhausted.

When cool the flask is weighed again. The weight is not altered. Chemical change has taken place, but no matter has been created or destroyed.

That chemical change takes place without loss or gain of matter can also be demonstrated by means of the apparatus shown in Fig. 28. The flask is fitted with a tight rubber cork through which pass a stout wire and a greased glass rod. To the wire is fastened a small candle. Touching the wick of the candle is a wax match, fastened to the wire. The whole apparatus is weighed. The cork, and all that

it carries, is then removed and the end of the glass rod heated. After the cork has been tightly replaced, the glass rod is pushed down until it touches the match, which ignites and lights the candle. When the apparatus is again cool, its weight is found to be unaltered.

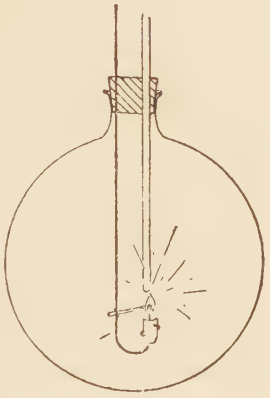


FIG. 28

Lavoisier did several experiments which showed that matter could not be destroyed or created. The experiment described on page 29 clearly showed this. The volume of air at the beginning of the experiment was 50 cubic inches, and at the end $42\frac{1}{2}$ cubic inches. The volume of the gas he obtained from the calx of mercury, or mercuric oxide, was $7\frac{1}{2}$ cubic inches. Therefore all the air used up was recovered. The mercuric oxide collected weighed 45 grains. From this he obtained $41\frac{1}{2}$ grains of mercury and $3\frac{1}{2}$ grains of oxygen. Nothing, therefore, had been lost or gained.

Thousands of experiments have been carried out since the time of Lavoisier, all proving directly or indirectly that matter is indestructible. Here, then, must be a great law of nature. It is called the **Law of the Conservation of Matter,** or the **Law of the Conservation of Mass.** It may be stated equally well: (1) *Matter is indestructible,* or (2) *Matter cannot be created or destroyed.*

PRACTICAL EXERCISES

(1) Try a separate mixture of copper filings and sulphur. Find out if a compound is produced when the mixture is heated.

(2) Find out if zinc, copper, and tin will give hydrogen when heated in a current of steam.

(3) Rub in a mortar 4 grams of mercury with 2.54 grams of iodine and a few drops of pure alcohol. Triturate until all the alcohol has evaporated. Determine whether the substance produced is a mixture or a compound.

CHAPTER IV

CARBON AND SOME OF ITS SIMPLE COMPOUNDS

Exp. 37—To observe the effect of heat on coal, sugar, wood, flour, etc., when the supply of air is limited

Required—Sugar, flour, small pieces of coal, wood, and bone; test-tubes, iron spoons

Directions—Heat in dry test-tubes, held horizontally, the substances provided. In each case note if a gas is given off, if the gas has a smell, is inflammable, or will allow substances to burn in it.

Notice also if any liquid products are obtained. Smell the liquid. Try whether it will affect litmus or burn.

Examine carefully the substance left behind. Is it the same in each case, and is the same proportion of residue obtained in each case?

The black substance is **carbon** in a more or less pure state.

To find whether it is pure, heat some of it in an iron spoon in the air. Carbon itself, as you know, burns in the oxygen of the air, giving carbon dioxide. The amount of ash left behind will show the amount of impurity in the carbon obtained from the various substances. Tabulate your results.

Exp. 38—To collect some of the gases obtained in the last experiment, and to compare them with coal gas

Required—Same substances as in Exp. 37; hard glass tubes, troughs, jars, lime-water, litmus

Directions—Fit a hard glass tube with cork and delivery tube; fill it half full of one of the substances provided, heat strongly and collect the evolved gas over water. If possible, collect several jars.

Find out the smell, solubility, heaviness or lightness of the gas.

Burn jars of the gas, and test the products with litmus and lime-water.

Now collect over water several jars of coal gas by means of india-rubber tubing connected to the gas tap. Do exactly the same experiments with the coal gas as you did with the gas you made. Tabulate your results.

Do you think that the two series of results are sufficient to show that coal gas is practically the same as the gases obtained on heating sugar, wood, etc., in absence of air?

Exp. 39—To try to obtain carbon dioxide by heating carbonates

Required—Calcium carbonate (powdered marble or limestone), sodium carbonate (washing soda), magnesium carbonate (magnesite); hard glass tubes, lime-water, glass rod

Directions—Heat strongly in a hard glass tube a small quantity of each substance. One quarter of a tubeful is sufficient. After heating for a short time, hold a glass rod, on which hangs a drop of lime-water, inside the top of the tube. Also try if gas is coming off by applying a lighted taper to the mouth of the tube.

In each case allow the tube to cool, scrape out some of the residue, and add a drop of water to it. Does it get warm or dissolve? Next, shake the residue with a few drops of litmus solution. Try the effect of litmus on the carbonates. Has the strong heating caused any alteration in the carbonate?

Exp. 40—To find the percentage loss of weight on heating calcium carbonate strongly

Required—Calcium carbonate (marble or calcite), muffle furnace, crucible and lid, balance, crucible tongs, quicklime

Directions—Weigh a clean, dry crucible and lid. Weigh into it one gram of powdered marble, and heat in the muffle furnace for half an hour. [A muffle furnace is shown in section in Fig. 29.] Cool, weigh, and again heat for a quarter of an hour. Repeat until two successive weights are the same. Calculate the percentage loss in weight.

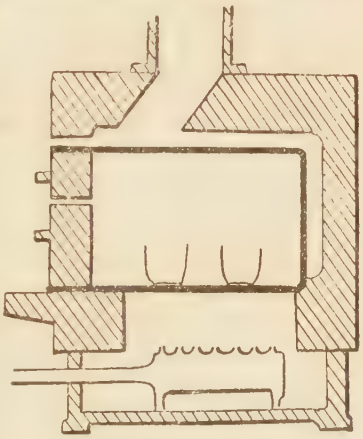


FIG. 29

Test the residue with water, litmus, and dilute hydrochloric acid, and compare its behaviour with that of quicklime.

Are calcite and marble changed to quicklime on strong heating?

Exp. 41—To observe the action of acids on carbonates

Required—Marble, limestone, chalk, magnesium carbonate, sodium carbonate; test-tubes, litmus, lime-water, dilute acids

Directions—Try the effect of dilute acids on each of the given carbonates.

Find out whether the gas given off has a smell, taste, colour, or an effect on litmus and lime-water.

See whether it will burn or allow a taper to burn in it.

Is the gas the same in every case?

Which of the substances would you use for the preparation of considerable quantities of the gas?

Exp. 42—To prepare carbon dioxide and examine its properties

Required—Marble, dilute hydrochloric acid; flask or bottle fitted with thistle funnel and delivery tube, large beaker, jars, troughs, balance

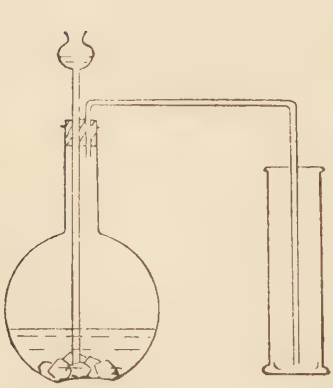


FIG. 30

Directions—Fit up the apparatus shown in Fig. 30.

Carefully slide down the side of the flask small pieces of marble and cover them with acid. Could you use any other carbonate?

Collect the gas by downward displacement of air. You can tell when each jar is full by applying a lighted splinter to the mouth of the jar.

Test the gas in the same way as in Exp. 41 and then carry out the following experiments:—

(1) Try if the gas is soluble by inverting a jar of it in water. Would it be possible to collect the gas over water?

(2) Try to burn a piece of magnesium ribbon in the gas.

(3) Try to pour the gas from one jar to another, and afterwards test each jar for the gas.

(4) Weigh a beaker, and then fill it with carbon dioxide from a dry jar. Is the weight altered?

Leave the uncovered beaker on the balance pan and observe the weight after a few minutes. Test the gas in the beaker for carbon dioxide. Try to explain your results.

(5) Pass the gas from the delivery tube through lime-water diluted with its own volume of water. What happens? Heat the liquid you obtain, and test the gas evolved with a drop of lime-water on a glass rod.

To the milky liquid left after boiling add dilute hydrochloric acid and again test the gas evolved. Is the milkiness due to a carbonate? What must that carbonate be?

Make a list of all the properties of carbon dioxide shown by your experiments, and answer all the questions asked.

Exp. 43—To examine the liquid residue from the preparation of carbon dioxide

Required—Residue, evaporating dish, copper sulphate

Directions—Pour off and filter if necessary the liquid obtained in the flask or bottle in Exp. 42, and evaporate down 30 or 40 c.c. of it in an evaporating dish on the wire gauze. Try to obtain crystals from some of it. Evaporate a second portion to complete dryness, and allow the dish to stand in the air. What happens?

Now make some white copper sulphate, and touch with it the residue which has stood in the air. Is there water present? If so, where can it have come from?

The residue is called calcium chloride. It is a salt, like those you obtained by dissolving metals in acids. Here, then, is a second method of obtaining salts. What is this method?

Calcium chloride is a **deliquescent** substance; that is, it takes up from the air enough water to dissolve it. If it takes up water from the air, would it not take up water from other gases? Could we not dry carbon dioxide by passing it through a tube containing recently heated calcium chloride?

Exp. 44—To find the volume of carbon dioxide that can be obtained from 1 gram of limestone, marble, or chalk

Required—Powdered limestone, marble, and chalk; dilute hydrochloric acid; small flask, short test-tube, cotton, gas jar, trough, balance

Directions—Fit up the apparatus shown in Fig. 23.

Into the flask put about 30 c.c. of dilute hydrochloric acid; weigh the short tube, and into it weigh about .6 gram of powdered limestone or marble or chalk; suspend it with cotton in the flask. When all is ready, loosen the cork, and

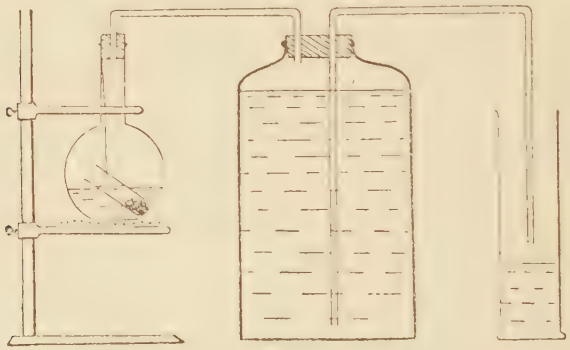


FIG. 31

let down the tube until its mouth is just above the acid. Replace the cork, and tilt or shake the flask so that the acid may act on the solid in the tube.

Collect and measure the carbon dioxide, and calculate the volume of gas obtained from 1 gram of marble, etc.

This method is subject to the error due to the solution of carbon dioxide in the water in the flask and trough.

The small test-tube and cotton may be replaced by a filter paper. See *Alternative Method, Exp.* 33.

A better apparatus is shown in Fig. 31. In the bottle the water is covered with a layer of paraffin oil, a liquid in which carbon dioxide is not soluble. The rest of the apparatus explains itself. Can you see a possible error in this method? There are two important sources of error. Try to find them out.

Exp. 45—To find the percentage by weight, of carbon dioxide in limestone, chalk, or marble

Required—Powdered limestone, chalk, or marble ; flask, balance, watch glasses

Directions—Into a flask put about 50 c.c. of dilute hydrochloric acid. Weigh the flask and acid. Weigh out on a watch glass, or smooth paper, about 3 grams of powdered limestone, chalk, or marble. Introduce this, a little at a time, very carefully into the flask, so that none is lost. Any solid sticking to the flask may, with a little care, be brought into contact with the acid by tilting the flask. When all the solid has dissolved in the acid, suck out the carbon dioxide in the flask through a glass tube, taking great care that the tube does not touch the wet glass or the liquid. If a drop of liquid is removed by the rod, your experiment will be spoiled. Weigh the flask and its contents.

Calculate the percentage loss of carbon dioxide.

What are the possible errors in this experiment ?

A better apparatus is shown in Fig. 32.

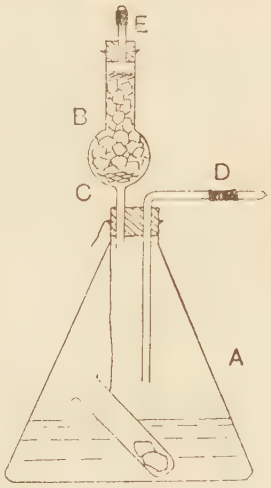


FIG. 32

A is a small flask with about 30 c.c. of dilute hydrochloric acid in it. Suspended in the flask by cotton is a small tube containing a weighed quantity of solid. **B** is a tube containing calcium chloride to dry the carbon dioxide given off, and cotton wool **C** to prevent the calcium chloride from falling into the flask. The tubes **D** and **E** are fitted with glass plugs.

About a gram of marble is weighed into the small tube, which is then suspended as shown in the figure. The whole apparatus is next weighed. Remove the plug **E** and tilt the flask until the acid acts on the marble in the tube. When all the marble is dissolved, the glass plug at **E** is replaced by a short piece of rubber tubing, the glass plug on **D** is removed,

and the carbon dioxide is sucked out of the flask. The whole is again weighed complete as in Fig. 32, and the percentage loss of carbon dioxide is calculated.

Are the results the same as those given by Exp. 40 ?

Suggest possible errors in the experiment, and methods of avoiding them. Compare your results with those obtained by boys who have used limestone or chalk. Do limestone, chalk, and marble contain equal amounts of carbon dioxide ? Can these results be said to prove that they are the same substance ?

Another experiment which would help to prove this would be to dissolve some of each substance in dilute hydrochloric acid, evaporate down the solution obtained, and see if the deliquescent calcium chloride was obtained from each.

Exp. 46—To observe the action of air and breathed-out air on lime-water

Required—Clock glasses, test-tubes, flask, glass tubing, and lime-water

Directions—(1) Put some clear lime-water on two clock glasses. Let one stand on your bench, and put the other on the window-sill outside the window. Is a scum formed more quickly on one than on the other ? Explain the result.

When the glasses have stood for some time, pour the liquid, etc., into a test-tube, and add dilute hydrochloric acid. Is carbon dioxide evolved ?

(2) Next, fit up and use an apparatus by means of which you can draw air through lime-water. What is the result ?

(3) Finally, put the end of a glass tube under lime-water contained in a test-tube, and blow through the glass tube. Is there more or less carbon dioxide in your breath than in the air ?

Exp. 47—To observe the effect of lime on washing soda (sodium carbonate)

Required—Flasks, filter, evaporating basin, slaked lime

Directions—You have proved that washing soda contains carbon dioxide, and that carbon dioxide forms a carbonate when passed through lime-water. Might it not be possible to transfer the carbon dioxide from a carbonate to lime without actually preparing carbon dioxide ?

Dissolve about 10 grams of washing soda in about 100 c.c. of water in a flask, and add to the solution about 5 grams of slaked lime.

Boil the mixture for some time. Filter ; wash the residue several times with hot water. Evaporate down the filtrate to dryness. Do not add the washings to the filtrate, or the evaporation will take too long.

Test the residue left on the paper with acid. Is it lime or calcium carbonate ?

Now test some of the residue in the evaporating dish with acid and with litmus. Is it washing soda or lime ? Does it destroy the acid properties of acids ? If so, try to obtain a salt from it. Let some of it stand in the air. Does it take up moisture ? Wet your finger and touch a small piece of the residue. What does it feel like ? The substance is caustic soda, and it is the same substance as that obtained by the action of sodium on water.

From your experiments it is evident that the carbon dioxide contained in the sodium carbonate has passed to the lime, and the lime has given its caustic properties to the soda.

Exp. 48—To study the action of acids on sodium carbonate and caustic soda

Required—Solutions of caustic soda, sodium carbonate, and hydrochloric acid ; litmus papers

Directions—Into a small flask put a few c.c. of caustic soda and a litmus paper. Add hydrochloric acid, a few drops at a time, shaking after each addition, until the litmus paper is just turned pink. Does the liquid still feel soapy ? Evaporate down the liquid and try to obtain crystals.

Repeat the experiment, using sodium carbonate solution instead of caustic soda. Add acid until the colour of the paper is a decided pink, not purple. Evaporate as before.

If no crystals can be obtained, evaporate to dryness. Are the solids obtained identical in appearance and taste ?

You have once more obtained a salt, namely, common salt. The sour taste of the acid and the sharp burning taste of the caustic soda have disappeared, and a salt with no action on litmus has been obtained. Caustic soda and sodium carbonate are said to be **alkaline** to litmus. Acids neutralise alkalis and give salts.

Carbon dioxide is an acid oxide. Will it neutralise caustic soda? See Exp. 49.

Exp. 49—To observe the action of carbon dioxide on caustic soda solution

Required—Carbon dioxide apparatus, caustic soda solution, litmus papers, lime-water, large test-tube, evaporating basin

Directions—Pass carbon dioxide for some time through about 20 c.c. of caustic soda solution contained in a large test-tube. Put a litmus paper in the solution. Does carbon dioxide neutralise caustic soda?

Next, warm the solution obtained. Test the gas given off for carbon dioxide. Could all the carbon dioxide given off have been simply dissolved in the liquid?

Evaporate the solution and try to obtain crystals. Test the crystals with acid and litmus, and compare them with washing soda crystals.

CARBON

Carbon, the substance obtained in Exps. 37 and 38, is contained in all animals and plants, and in most of the substances derived from them. The form of carbon obtained from wood is called *charcoal*. You should have noticed that this form is not crystalline. The carbon obtained from bones was much harder than charcoal, and left very much more ash when heated in the air. It is called *animal charcoal*. Still another form of carbon was that obtained from coal, namely, *coke*. Soot, lamp black, gas carbon, diamond, and graphite are all forms of carbon, more or less pure. They will be studied later. Any one of these forms of carbon, when heated in oxygen, burns and gives carbon dioxide.

CARBON DIOXIDE

Your experiments have shown you that carbon dioxide is driven off when limestone and chalk and marble are heated, and that the same weight of carbon dioxide is contained in each of these substances. But you should also have found out that soda, *i.e.* sodium carbonate, does not give off carbon dioxide when heated. The substance left behind, when limestone, etc., is heated in a muffle furnace, resembles quicklime

in its properties. Again, limestone, marble, and chalk give off the same percentage weight of carbon dioxide when treated with dilute hydrochloric acid, and the liquor left in each case gives the same substance, calcium chloride, on evaporation to dryness. It is evident, therefore, that limestone, chalk, and marble are simply different forms of the same substance.

Carbon dioxide, the gas obtained from these and other carbonates, you have found to be a colourless gas with a sharp taste and practically no smell. It is heavier than air, and can therefore be collected by downward displacement of air. It is slightly soluble in water, giving a solution with a sharp acid taste. It is acid to litmus.

It will not burn, and will not allow ordinary combustibles to burn in it. Magnesium, however, burns in it, and produces magnesium oxide and little black specks of carbon. That carbon dioxide consists of carbon and oxygen only is shown by the fact that carbon dioxide is formed when carbon is burnt in oxygen. The magnesium, therefore, must split up the gas into carbon and oxygen, and burn in the oxygen set free.

When a dilute solution of sodium carbonate is treated with lime, the carbon dioxide in the soda is transferred to the lime, making calcium carbonate and a new substance, caustic soda. The latter is a solid which really takes up water from the air, is soapy to the touch, and which will combine with carbon dioxide, giving sodium carbonate. It was Dr. Black of Edinburgh who, in the middle of the eighteenth century, first explained the change of *mild alkali*, *i.e.* sodium carbonate into *caustic alkali*, *i.e.* caustic soda. He showed that the sodium carbonate lost the carbon dioxide which the lime gained, and that the caustic property of the lime was transferred to the soda. The term **alkali** (Arabic, *al-qali* = *the ash of the plant from which soda was first obtained*) is still used for substances which turn red litmus blue. The word caustic (Greek $\chi\alpha\acute{\iota}\sigma\omega$ = shall burn) is used for substances which burn or corrode animal and vegetable matter.

Acids and alkalis, as you have seen, neutralise one another, and give salts which have no acid or alkaline properties. Other substances will also neutralise acids and give salts. If more zinc than will dissolve is put into dilute sulphuric acid, and left until no more hydrogen comes off, it will be

found, on filtering off and evaporating the liquid, that a salt called zinc sulphate, which is not acid to litmus, is produced. Again, if more chalk than will dissolve is put into hydrochloric acid, and the liquid is filtered, the solution obtained is not acid to litmus after the dissolved carbon dioxide has been boiled off. This solution when evaporated to dryness deposits the salt calcium chloride. Evidently, therefore, the properties of acids can be destroyed by substances other than alkalis.

HARDNESS OF WATER

Carbon dioxide turned lime-water milky. The solid causing the milkiness was afterwards found, by testing with hydrochloric acid, to be chalk. When carbon dioxide was passed into diluted lime-water for some time, the milky liquid first obtained became clear again, owing to the formation of a soluble substance composed of chalk, carbon dioxide, and water. This soluble substance is called calcium bicarbonate. When the solution of calcium bicarbonate was warmed, the carbon dioxide holding the chalk in solution was given off, and chalk was once more precipitated.

These facts are useful for explaining the presence of *temporary hardness* in natural water. Carbon dioxide is contained in air to the extent of about one part in 3000 parts of air. This carbon dioxide dissolves in rain, river, and spring water. When water containing carbon dioxide comes into contact with limestone, it dissolves some of the limestone, giving calcium bicarbonate. The calcium bicarbonate reacts with soap, giving a curd. Until all the calcium bicarbonate has been used up a lather cannot be obtained. In such a case we say that the water is *hard*. If the hardness in a particular water were due to this bicarbonate alone, the water could readily be softened by boiling. Boiling breaks up the bicarbonate into chalk, water, and carbon dioxide. The carbon dioxide is given off. The chalk, when no longer in solution, has no effect on soap; therefore the water at once gives a lather with soap. *This kind of hardness is called* **temporary,** *because it can be removed by boiling.* Another way of removing the hardness is to add lime. The lime combines with the extra carbon dioxide present, forming chalk, and consequently the chalk which was kept in solution by this extra carbon dioxide is precipitated.

You may have noticed that a kettle becomes coated inside, after being in use for some time, with a greyish stony substance called "fur." This "fur" is largely calcium carbonate, which has been deposited on the kettle when the carbon dioxide holding it in solution has been driven off by the constant boiling of the water. Engine boilers, in districts in which the water contains chalk, become coated with a thick layer of this substance. They have therefore to be freed from it periodically, in order to prevent waste of heat and injury to the boiler by the fire.

The expression "temporary hardness" is necessary to distinguish this kind of hardness from that due to gypsum and other substances. These substances cause hardness which cannot be removed by boiling. Such hardness is called **permanent hardness.** The latter is not a very good term, because permanent hardness can be removed by the addition of soda to the water or by distilling the water. See pp. 361 and 362.

BREATHING OF ANIMALS

You have discovered that there is more carbon dioxide in the air of the laboratory than there is in the air outside. This excess is partly due to the burning of coal gas in the bunsen burners. You have also found that your breath contains much more carbon dioxide than is contained in ordinary air. Some of the carbon dioxide in the air of the laboratory must therefore have come from your breath. You have found that bones contain carbon, and you have been told that all animal substances contain carbon. Consequently, the extra carbon dioxide in your breath must come from your body.

In the blood is a substance called *hæmoglobin*, possessing the power of combining with oxygen to give *oxyhæmoglobin*, which gives blood its red colour. When air is breathed in, it enters the air-cells of the lungs, and there comes into contact with the blood as the latter passes through innumerable tiny veins. The hæmoglobin becomes oxyhæmoglobin, and the blood flows to the heart, by which it is pumped through the large arteries into smaller arteries, and thence into little blood-vessels so numerous that you cannot prick your skin with a needle without puncturing one of them. The oxyhæmoglobin gives up its oxygen to the waste-products of

the muscles, etc., and converts the carbon of the waste into carbon dioxide. The blood, therefore, loses its bright red colour and becomes darker. The carbon dioxide is carried away by the blood, first to small veins, then into large ones, and finally back to the lungs, where it passes into the air and is breathed out. That the muscles do not waste away is due to the fact that the food eaten is converted in the stomach into substances which are carried by the blood to renew and even strengthen the muscles used.

Fish breathe in water containing dissolved oxygen, and use the oxygen in the same way as land animals use the oxygen of the air. A fish put into water which has been recently boiled and cooled, quickly dies from lack of oxygen.

Besides the carbon dioxide sent into the air by burning and breathing, much of this gas is produced by the decay of animal and vegetable matter, and a still larger quantity issues from cracks and fissures of the earth. In spite of this, the percentage of carbon dioxide in the air does not increase. What can happen to the carbon dioxide? Does it escape from the earth's atmosphere into space, or is it used up in some way?

PLANTS AND CARBON DIOXIDE

Van Helmont of Brussels, who lived from 1577 to 1644, believed that plants consisted entirely of water. To prove this he planted a willow weighing 5 pounds in a large earthenware vessel containing 200 pounds of dried earth. He watered this tree for five years with rain and distilled water and then pulled it up. He found that it weighed 169 pounds and 3 ounces, and that the earth in the vessel had decreased in weight by 2 ounces only. He thought, therefore, that 164 pounds of root, leaves, etc., had been produced from water. He would probably have been very much astonished if he had been told that the greater part of the willow was derived, not from the water, but from the air.

If a water plant or weed, *e.g.* watercress, is tied to a stone and placed in water in an apparatus like that shown in Fig. 33, it will be seen, on exposing it to sunlight for some time, that bubbles of gas are given off from its leaves. These bubbles, when tested, are found to be oxygen. The oxygen comes from the carbon dioxide dissolved in the water.

Both water and land plants have the power of taking in carbon dioxide from the air (or from water in the case of water plants) through their leaves. With the help of sunlight and a green substance called *chlorophyll*, they can make use of the carbon dioxide. The carbon they retain to build up their structure; the oxygen they give back to the air, wholly or partly.

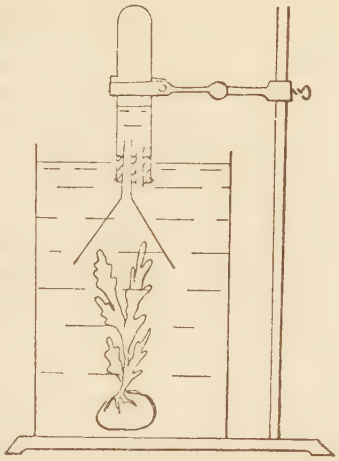


FIG. 33

The consequence of this action of green plants is the keeping of a balance in the quantity of oxygen and carbon dioxide in the air. Burning, the breathing of animals, decay, etc., use up oxygen and increase the proportion of carbon dioxide; plants, on the other hand, use up carbon dioxide and give back oxygen.

Do not think that plants are composed entirely of carbon! They contain also much hydrogen, oxygen, and nitrogen, together with some sulphur, phosphorus, and mineral matter. Compounds of these substances in solution in water are taken up by the roots of the plants. It has recently been shown that some plants, *e.g.* the pea tribe, are able, with the help of certain bacteria, to take up nitrogen direct from the air.

Decay of vegetable and animal matter is due to the existence of other bacteria which feed on the dead plant or animal, and gradually convert it into carbon dioxide and other products in a manner somewhat similar to that in which higher animals dispose of their food.

We realise somewhat from the above facts that Nature is an excellent manager. Huge forests and luxuriant plant life are mainly built up out of a gas present in the air in the proportion of only one part to 3000 parts of air. These forests and plants die and decay, giving back the gas to the air. Some of the dead vegetable matter may be buried by the sand of the sea, and become compressed and changed into coal. Another part may be burned. Still another part may be

eaten by animals. The end is always the same. Coal is discovered and burnt by man, and carbon dioxide is given back to the air; the animal uses up its food and breathes out much of it as carbon dioxide; the burning wood produces carbon dioxide, and the decay of the wood, although slow, also gives back carbon dioxide to the air. The result is that the proportion of carbon dioxide in the air has not altered in the slightest degree since the composition of the air was first accurately determined.

PRACTICAL EXERCISES

(1) Find the percentage weight of carbon dioxide in magnesite.

(2) Find the weight of carbon dioxide that can be obtained from one gram of carbon.

Method.—Pass oxygen over a known weight of charcoal heated in a hard glass tube. Absorb the carbon dioxide produced in caustic soda solution.

CHAPTER V

COMBUSTION, FLAME, ETC.

Exp. 50—To find out if substances begin to burn at different temperatures

Required—Phosphorus, carbon bisulphide, wire gauze, test-tube, filter paper, glass rod, evaporating dish

Directions—

(1) Warm a glass rod slightly and touch with it a small piece of yellow phosphorus contained in a dish.

(2) Touch a piece of sulphur with the same glass rod. Does it light?

(3) Heat the glass rod more strongly and hold it in the vapour of carbon bisulphide contained in an evaporating dish. *Only a few drops of carbon bisulphide should be used.*

(4) Dissolve a small piece of yellow phosphorus in a few drops of carbon bisulphide and pour the solution on to a filter paper placed on a retort stand ring. What happens when the carbon bisulphide has evaporated? Explain the result.

Caution—On no account must the solution of phosphorus be allowed to touch your fingers, books, or clothes.

(5) Hold a glowing splinter in a stream of coal gas. Does the gas light?

(6) Light a bunsen burner and press down on the flame a

piece of wire gauze. What happens when the gauze gets white hot? Explain the result.

(7) Turn out the bunsen burner, hold a piece of gauze about an inch above the top of the burner and light the gas which passes through the gauze. Now slowly raise the gauze. What happens to the flame?

What conclusions may be drawn from these experiments?

Exp. 51—To examine a candle flame

Required—Candle, piece of glass tubing drawn out to a jet, platinum wire, paper rubbed with mercuric iodide, blow-pipe.

Directions—

(1) Draw a candle flame and try to distinguish its various parts. Note the bending over of the wick. Explain why and how it is made to bend.

(2) Hold a piece of platinum wire in various parts of the flame, and so determine roughly the relative temperature of each part.

(3) With the help of a glass tube drawn out to a jet, try to draw off and light gas from various parts.

(4) Cool the flame by pressing down on it some cold object, such as the bottom of a retort stand or a porcelain dish filled with water. Does the flame give more or less light? Examine the iron or the dish. What is the black deposit, and how would you prove it to be what you think that it is?

(5) Press down on the flame a piece of white paper rubbed with mercuric iodide, and quickly withdraw the paper before it lights. Mercuric iodide turns yellow when heated. Does the flame heat the paper evenly?

(6) Blow air through the flame by means of a mouth blow-pipe, and notice whether the flame becomes more or less luminous. Also try with the platinum wire whether the jet of flame is hotter or cooler than the ordinary candle flame.

(7) Finally, fit a test-tube with a cork and jet, put into it a few scrapings of wax from the candle, heat the wax strongly in the bunsen, and light the gas coming out of the jet. Is the flame like that of a candle?

Exp. 52—To examine a bunsen flame

Required—The same substances as in Exp. 51

Directions—Draw a bunsen burner. Repeat experiments

(1) to (6) of Exp. 51 with the bunsen flame, firstly with the air holes of the burner closed and secondly open.

Also put a pin through a match close to the match head; balance the pin on the top of the tube of the unlighted burner, so that the match head is above the centre of the tube, and light the burner. Account for the result.

Compare your results with those obtained with the candle flame. Draw conclusions as to the causes of luminosity.

TEMPERATURE OF IGNITION

Your experiments have shown you that various substances take fire at very different temperatures. Phosphorus, which has been deposited in a finely divided state on a filter paper from solution in carbon bisulphide, takes fire at the ordinary temperature. Carbon bisulphide takes fire at a somewhat higher temperature; a glowing chip will not ignite coal gas; thin iron wire requires to be heated to whiteness in a bunsen before it will burn in the air. The temperature at which a substance takes fire is called the **temperature of ignition** of that substance.

FIG. 34

COMBUSTION

A substance which is burning is said to be undergoing combustion. **Combustion** may be defined as chemical union accompanied by evolution of light and heat. The substance which burns is said to be **inflammable** or **combustible.** The gas which allows combustion to take place in it is called a **supporter of combustion.** But substances which are concerned in burning cannot very well be classed into combustibles and supporters of combustion, because gases which are generally known as supporters of combustion can readily be made to burn in gases which are combustible.

The apparatus shown in Fig. 34 can be used to show that air will burn in coal gas. A lamp glass is fitted at the bottom with a cork carrying a wide glass tube and a narrow delivery

tube, and at the top with a cork carrying a fairly wide glass tube. Coal gas is passed into the apparatus for a minute or two. It is then lighted at **A** and **B**. The coal gas is next gradually turned off until the flame at **B** travels through the tube **BC** and remains at **C**. That the flame at **C** is due to air burning in coal gas can be shown by closing **B** with the finger. Air can no longer enter, and the flame at **C** goes out.

Similarly a jet of air can be burnt in an inverted jar of hydrogen which has been lighted at the bottom. Oxygen can be burnt in sulphur vapour by lowering a jet, from which oxygen is slowly issuing, into a large test-tube containing boiling sulphur, the sulphur vapour being lighted at the top of the boiling tube.

It is evident that the terms *combustible* and *supporter of combustion* must be carefully used. Carbon dioxide will not support the combustion of a taper, sulphur or phosphorus, but it will allow magnesium to burn in it. When, therefore, a gas is said to be a supporter of combustion, the substances which burn in it should be mentioned.

FLAME

Flames consist of intensely heated gases, and they frequently contain small incandescent particles of solids. [A substance is said to be *incandescent* when it is hot enough to give out light.]

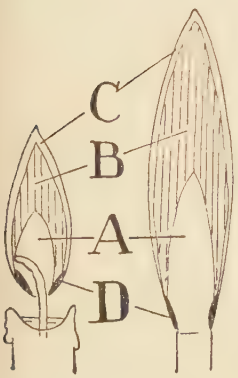


FIG. 35

Fig. 35 represents the flame of a candle and the flame of coal gas burning from a round jet. In each case **A** represents the zone of unburnt gases, **B** the luminous zone, **C** a narrow non-luminous zone, and **D** a small blue zone. The conical shape of the flame must be due to the fact that air does not immediately come into contact with all the gas formed round the wick or issuing from the top of the tube. The unburnt gas rises until it meets air, when it burns. This continues until a hollow cone is formed. The luminous zone **B**, as you have discovered, contains carbon and is very hot. The non-

luminous zone **C** contains no solid carbon, and is about as hot as **B**. In this zone are burnt up those gases which escape from **B**. The non-luminosity of this zone is due partly to the cooling action of the air which is constantly being drawn into the flame to supply oxygen for the combustion of the coal gas, and partly to the nature of the burning gases. In the blue region **D**, the gas is being partly burnt to water and partly converted into hydrogen and a gas called carbon monoxide.

You have proved for yourselves that cooling lessens the luminosity of a flame. Luminosity is lessened also by decreasing the pressure on a flame. A candle will not give so much light at the top of a high mountain as at sea level. The effect of pressure can be shown experimentally by burning a candle under the bell jar of an air pump, and pumping out air until the candle gives little light. When air is again admitted, and the pressure thereby increased, the candle burns more brightly. Lime should be present to absorb the carbon dioxide produced by the burning of the candle.

When air was admitted through the holes of a bunsen burner the luminosity of the flame was almost entirely destroyed. This was due to three causes: firstly, sufficient oxygen was provided to burn up the gas without the formation of solid carbon; secondly, the drawn-in air diluted the gas; thirdly, the air exerted a cooling action on the flame. The presence of solid matter in a flame is a very important cause of luminosity. The incandescent gas light is produced by an ordinary bunsen flame in which is suspended a mantle composed of solids which glow brightly when heated.

Luminosity, then, is caused by presence of solid matter, increase of pressure, increase of temperature (cooling caused decrease in luminosity), or by a combination of these causes.

THE DAVY LAMP

You discovered that a bunsen flame would not pass through ordinary wire gauze until the gauze became almost white hot. This fact is taken advantage of in the construction of the Davy lamp, which is much used in coal mines. In this oil lamp all the openings by which air can reach the flame are covered with fine wire gauze. Consequently the flame cannot pass from the inside to the outside, even when the lamp is

placed in an explosive mixture of gases. In coal mines an explosive mixture of marsh gas and air is sometimes present. In such cases the miner sees his flame become less luminous, bluish in colour, and much larger. No explosion can take place, however, unless a strong draught causes the flame to touch the wire gauze and heat it above the temperature of ignition of the marsh gas, or an explosion in another part of the mine drives the flame through the gauze. A lamp is shown in section in Fig. 36.

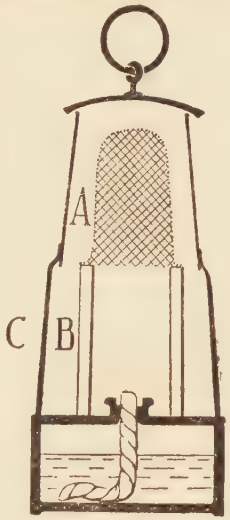


FIG. 36

A = Fine wire gauze.
B = Glass.
C = Metal rods supporting the metal cap which protects the gauze.

PRACTICAL EXERCISES

(1) Prove that carbon dioxide and water are produced when a candle burns.
(2) Prove that carbon dioxide and water are produced when coal gas burns.

CHAPTER VI

STUDY OF SALT, ETC.

Exp. 53—To prepare hydrochloric acid gas and examine its properties

Required—Common salt or rock salt, strong sulphuric acid, apparatus shown in Fig. 37, sulphur, sodium, phosphorus, dry gas jars, test-tubes, litmus, carbonates, lime metals, deflagrating spoon

Directions—Warm some salt with strong sulphuric acid in a test-tube and note the colourless, fuming gas given off. This is called gaseous hydrochloric acid.

Now fit up the apparatus shown in Fig. 37. In the flask put rock salt or common salt. Add about 40 c.c. of strong sulphuric acid to about 20 c.c. of water, stirring during the addition. Pour the diluted acid down the thistle funnel until the salt is covered. Warm if necessary. Collect by downward displacement of air.

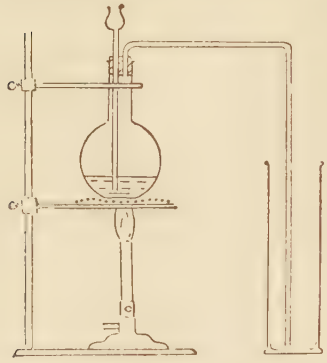


FIG. 37

Find out the smell, taste, solubility of the gas, whether it will burn or support the combustion of ordinary substances, *i.e.* a taper, sulphur, phosphorus, magnesium, sodium ; and note its action on lime-water and litmus. Explain its fuming in the air, and when you blow into it.

Next make a solution of the gas by passing it, for some minutes, into a small flask half full of water. Compare the action of this solution with that on your bench labelled dilute hydrochloric acid. Try the action of both on litmus, lime, sodium carbonate, calcium carbonate, silver nitrate solution, zinc, and other metals. Are the solutions identical in properties ?

Make a list of the properties of hydrochloric acid.

Pour out the residue from the flask and allow it to cool in a beaker or evaporating dish. What are the crystals ?

Exp. 54—To try to obtain hydrogen from gaseous hydrochloric acid

Required—Hydrochloric acid apparatus, trough, hard glass tube, corks, glass tubing, boat, iron filings

Directions—Fit up the apparatus shown in Fig. 38. Put some iron filings into the boat and place the latter in the glass tube. Pass gaseous hydrochloric acid from an apparatus which has been going sufficiently long to drive out the air from the flask. Heat the hard glass tube strongly. Collect the evolved gas in a test-tube over water and test whether it is hydrogen.

Exp. 55—To observe the action of gaseous hydrochloric acid on heated oxides and peroxides

Required—Apparatus shown in Fig. 38, without the part on right of **B**; *copper oxide, mercuric oxide, lime, lead peroxide, manganese dioxide, litmus papers, nitric acid, silver nitrate solution*

Directions—Into the hard glass tube, or into a boat as before, put a small quantity of the oxide. Pass hydrochloric acid

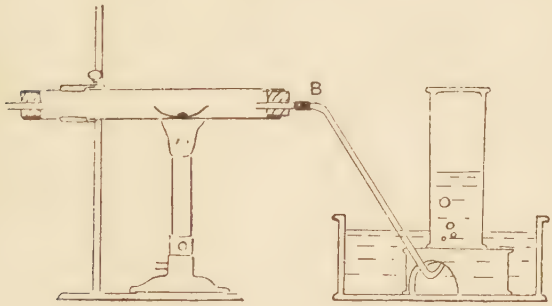


FIG. 38

and heat. Try the experiment with as many oxides as possible, taking care to use at least one oxide and one peroxide.

Test any gas given off with wet litmus paper and by smell. Test any liquid formed in the cool parts of the tube with white copper sulphate. What has happened to the oxides and peroxides.

Warm some of the solid residue with water in a test-tube, filter if necessary, and add to the clear solution a few drops of nitric acid and a solution of silver nitrate. Is a similar precipitate produced in each case? What can the precipitate be?

Can the greenish gas you obtain in some cases come from the oxides used, or must it come from the hydrochloric acid? Give reasons for your answer. The gas is called **chlorine**. Would it be possible to use a solution of the hydrochloric acid, instead of the gas itself, in order to prepare chlorine?

Exp. 56—To prepare chlorine and study its properties

Required—Manganese dioxide, strong hydrochloric acid solution, flasks, tubing, gas jars, taper, phosphorus, antimony, sulphur, magnesium, sodium, litmus paper, turkey-red cloth, turpentine

Directions—Fit up the apparatus shown in Fig. 39.

The apparatus should be used in a draught chamber.

In **A** put about 20 grams of manganese dioxide and moisten it thoroughly with a few c.c. of water. This is done to prevent danger of cracking when the flask is heated. [Explain how this danger of cracking arises.] The addition of water also to some extent prevents frothing, if powdered manganese dioxide is used.

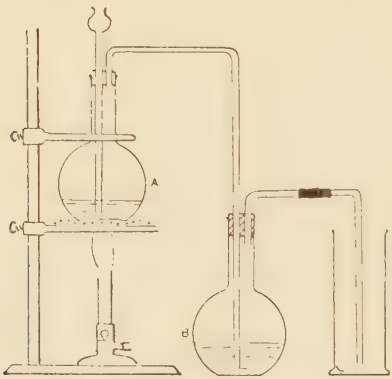


FIG. 39

The flask **B** contains water. Why?

Next introduce strong hydrochloric acid into **A** and gently warm. Collect several jars of chlorine, cover them with glass plates, and test them at your own bench.

Caution—Chlorine is very injurious if inhaled.

(1) Try whether chlorine is soluble in water.

(2) Into a jar put dry litmus paper, dry turkey-red cloth, a piece of paper covered with dry writing ink, and a second piece of paper with print on it.

(3) Into another jar put pieces of the same substances moistened with water. Allow both jars, covered with glass plates, to stand for some minutes. Note any changes.

(4) Try whether chlorine will bleach coloured flowers.

(5) Introduce into a jar a piece of unlighted phosphorus in a deflagrating spoon.

(6) Throw powdered antimony into another jar.

(7) Finally, moisten a filter paper with turpentine and introduce it into a jar. What are the products?

Examine the products formed in each case of combustion in any way you can think of.

Write a full account of your experiments, and try to explain the results. Make a list of the properties of chlorine.

Exp. 57—To obtain hydrochloric acid from chlorine and hydrogen

Required—Chlorine apparatus, hydrogen apparatus, glass tube drawn out to a jet, gas jar

Directions—Fill a large gas jar with chlorine. Into the jar introduce a jet of burning hydrogen. As soon as the hydrogen ceases to burn, remove the glass jet and smell the gas in the jar; next cover the jar with a glass plate and shake up the gas with a few c.c. of water. Test portions of the solution for hydrochloric acid with litmus, sodium carbonate, and silver nitrate solution.

HYDROCHLORIC ACID

In Exp. 53 you prepared gaseous hydrochloric acid by means of the apparatus shown in Fig. 37. The gas collected would not be quite dry, and would contain small quantities of sulphuric acid, salt, and sodium sulphate from the flask. The gas may be dried and purified by passing it through strong sulphuric acid. Fig. 40 shows an apparatus by means of which pure gaseous hydrochloric acid may be obtained and collected.

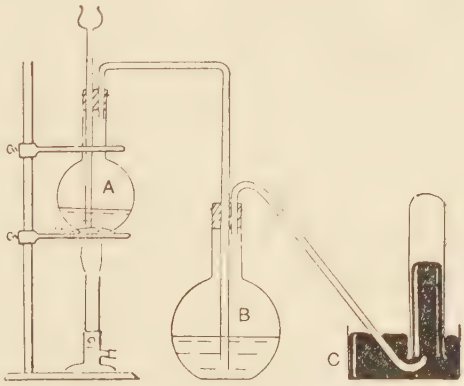


FIG. 40

A contains salt and sulphuric acid.
B contains strong sulphuric acid.
C contains dry mercury.

Priestley was the first to collect gaseous hydrochloric acid over mercury. The solution had been prepared by Glauber as early as 1650. Sodium sulphate, the salt which crystallises from the residue in Exp. 53, is still often called Glauber's salt, after Glauber its discoverer.

You have discovered that hydrochloric acid is a colourless gas with a sharp smell and sour taste, acid to litmus, and very soluble in water. The solubility may be strikingly shown by means of the following experiment. A dry, round-bottomed flask, fitted with a cork and jet as in Fig. 41, is filled with dry hydrochloric acid gas, and is inverted in a basin of water coloured by blue litmus. The flask is gently warmed to drive out some of the gas and then is allowed to cool. The first few drops of water entering the flask dissolve nearly all the gas, so that the pressure inside the flask is greatly reduced. The pressure of the air on the water in **A** forces it up as a fountain-like jet into the flask, and the blue colour of the water is changed to red.

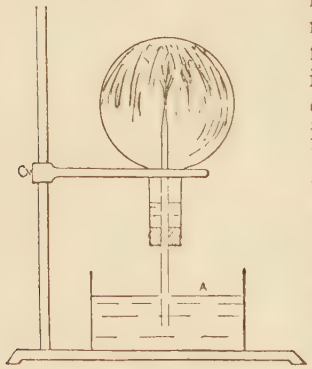


FIG. 41

One c.c of water at 0° C. will dissolve about 500 c.c. of hydrochloric acid gas. The strong solution smells of the gas.

As you have learned earlier, hydrochloric acid will neutralise bases, giving salts and water. Chalk and lime, for example, neutralised hydrochloric acid, giving calcium chloride in each case. All the salts obtained from hydrochloric acid by its action with metals, or metallic oxides, or carbonates, are called *chlorides*.

Thus, magnesium dissolves in hydrochloric acid solution, giving magnesium chloride and hydrogen. Zinc oxide dissolves in hydrochloric acid, giving zinc chloride and water. Sodium carbonate dissolves in the acid, giving sodium chloride, carbon dioxide, and water. Each of these chlorides, when dissolved in water and treated with silver nitrate solution, gives a white precipitate of silver chloride.

Exp. 54 showed clearly that hydrochloric acid gas contains

hydrogen. Ferrous chloride and ferric chloride are the substances left in the boat.

Exp. 55 should have shown you that metallic oxides with gaseous hydrochloric acid give water and solid substances quite different from the oxides used. The solid substance dissolves in water, giving a solution which precipitates silver chloride from silver nitrate solution. The solid must be a chloride. Gaseous hydrochloric acid, therefore, reacts with metallic oxides, giving chlorides and water.

When, however, a peroxide was used, a chloride, water, and chlorine were formed. The chlorine must have come from the hydrochloric acid, because metallic peroxides contain only oxygen and a metal. Hydrochloric acid must therefore contain both hydrogen and chlorine. Do these experiments show that hydrochloric acid contains only hydrogen and chlorine, or might the acid also contain other elements ?

CHLORINE

You readily obtained chlorine by warming manganese dioxide with strong hydrochloric acid solution. The gas was washed with a small quantity of water to free it from hydrochloric acid. Some of the chlorine dissolved in the water, giving it the greenish colour of the gas, but the whole of the very soluble hydrochloric acid gas was dissolved by the water. Chlorine is often made by warming a mixture of salt, strong sulphuric acid, and manganese dioxide. The hydrochloric acid formed from the salt and sulphuric acid at once attacks the manganese dioxide and gives chlorine.

Chlorine, when inhaled, irritates the lining of the nose and throat, so much that all the symptons of a violent cold are produced. Inhaled in larger quantities it produces death.

Chlorine is very energetic. Phosphorus and powdered antimony take fire and burn in it. Sodium and magnesium burn vigorously in it, forming common salt and magnesium chloride respectively. A taper burns in it with a smoky flame. Charcoal and sulphur will not burn in it.

If a jet of hydrogen be lighted and lowered into a jar of chlorine, it goes on burning and a fuming gas smelling like hydrochloric acid is produced.

If equal volumes of chlorine and hydrogen are mixed together and exposed to sunlight or the light from burning magnesium, or if a lighted taper is applied to the mixture, a

violent explosion takes place, hydrochloric acid gas and nothing else being produced. Hydrochloric acid gas can therefore be made from hydrogen and chlorine, and consequently can contain nothing but these substances.

Chlorine takes hydrogen from many substances containing it. Turpentine contains carbon and hydrogen. If a piece of filter paper be moistened with turpentine and dropped into a jar of chlorine, the chlorine combines with the hydrogen of the turpentine so vigorously that enough heat is produced to light the turpentine. The jar is afterwards found to be filled with hydrochloric acid gas and blackened with carbon. A wax taper burns in chlorine with a very smoky flame. The chlorine combines with the hydrogen in the wax and sets free the carbon as black smoke.

Chlorine can even take out hydrogen from water. If a solution of chlorine water in an inverted jar is exposed to sunlight, in the course of some days the colour of the chlorine disappears, oxygen collects in the jar, and hydrochloric acid remains in solution.

The bleaching action of chlorine is due to combination of chlorine with the hydrogen of water. Dry litmus paper, dry writing ink, and dry turkey-red cloth are not bleached by chlorine. The paper or cloth used must be thoroughly dried, and the chlorine must also be dry. When, however, these substances are wetted, the oxygen set free from the water by the chlorine combines with the colouring matter of the ink, litmus, flowers, or cloth, giving colourless substances. All these substances are constantly exposed to the oxygen of the air, but they are not bleached by it. It is evident, therefore, that the oxygen formed by the action of the chlorine is more active than ordinary oxygen. The oxygen is, in this case, said to be **nascent** (*i.e.* being born). Generally speaking, only substances coloured by vegetable colouring matters are bleached by chlorine. Printer's ink, which consists mainly of carbon in the form of lamp black, is not acted on by chlorine.

PRACTICAL EXERCISES

(1) Find the weight of a litre of hydrochloric acid gas.

(2) Boil a solution of hydrochloric acid for ten minutes and find out all the gas has been expelled from the solution.

(3) Find out if chlorine is completely expelled from solution in water by boiling.

CHAPTER VII

PROPERTIES OF GASES

Exp. 58—To find the weight of a litre of hydrogen

Required—Apparatus for making, purifying, and drying hydrogen; large flask fitted with rubber cork; balance

Directions—Dry a half-litre flask thoroughly by warming it above the bunsen flame and blowing out the moist air with bellows. When the flask is **quite cold**, cork it with a rubber cork and weigh it full of air. Next, fill the flask with pure dry hydrogen by upward displacement of air. The hydrogen should be passed into the flask for at least ten minutes in order to drive out the air completely. Slowly withdraw the tube from the flask, and cork immediately. Weigh the flask again. Now find the volume of the flask by filling it with water and measuring the water.

Let the volume be V c.c. One c.c. of air weighs about .00129 grams.

Weight of flask and air . .	=	grams.
Weight of air = V × .00129 . .	=	grams.
∴ Weight of empty flask . . .	=	grams.
Weight of flask and hydrogen .	=	grams.
Weight of empty flask . . .	=	grams.
∴ Weight of V c.c. of hydrogen . .	=	grams.

Calculate the weight of 1000 c.c. of hydrogen.

Answer the following questions and give reasons for your answers:—

(1) Why must the flask be quite cold before it is weighed full of air?

(2) Should you get the same weight for a litre of hydrogen on a cold and on a hot day?

(3) Should you get the same weight for a litre of hydrogen on days when the barometer is high and when it is low?

Exp. 59—To find the change in volume of a given mass of gas between the temperatures 0° C. and 100° C.

Required—Dry flask fitted securely with india-rubber cork carrying a short piece of glass tubing fitted with a piece of india-rubber tubing and clip; large water bath or tin can, test-tube holder, ice

Directions—Place the dry flask, full of air, in a vessel of boiling water in the position shown in Fig. 41A.

Hold down the flask for a few minutes with the clip open. To do this, use a test-tube holder or any means which may suggest itself to you. Then close the clip securely, and when the flask has cooled somewhat immerse it completely for a minute or two in a large vessel filled with ice and water, that is, in water at a temperature of 0° C. Open the clip.

FIG. 41A

Now take out the flask, remove the cork, and measure the water that has entered the flask. Find the volume of the flask by filling with water up to the cork. Measure the water. Subtract the volume of water which entered when the flask was cooled from the volume of the flask. You find thus the volume of air left in the flask at 0° C. This air completely filled the flask at 100° C.

Calculate the increase in volume of 1 c.c. of air at 0° C. when the temperature is raised through 1° C.

The experiment may be repeated with the flask full of other gases, such as oxygen, hydrogen, nitrogen, introduced by displacement of air. When the experiment is carried out with these gases, the clip should only be opened once or twice while the flask is being heated, and also just before the flask is taken out of the boiling water. This precaution is taken in order to prevent the mixing of air with the gas in the flask.

Do other gases give the same results as air?

Suppose the volume of the flask to be 186 c.c., and the volume of the water which entered 50 c.c.

Volume of a given mass of air at 0° C. = 136 c.c.
Volume of a given mass of air at 100° C. = 186 c.c.

$\therefore$ 136 c.c. of air at 0° C. expand 50 c.c. on being heated to 100° C.

$\therefore$ 1 c.c. of air at 0° C. expands $\frac{50}{136}$ c.c. on being heated to 1° C.

$\therefore$ 1 c.c. of air at 0° C. expands $\frac{50}{136 \times 100}$ c.c. on being heated to 1° C.

$$= \frac{1}{272}$$

That is, 1 c.c. of air on being heated from 0° C. to 1° C. expands $\frac{1}{272}$ of its volume at 0° C. Note—The true value is almost exactly $\frac{1}{273}$.

Exp. 60—To observe and measure the effect of pressure on the volume occupied by a gas

Required—Boyle's Law apparatus

Directions—Fig. 42 shows a Boyle's Law tube. This consists of a piece of uniform glass tubing bent into the form of a J. The short limb is closed; the long limb is open.

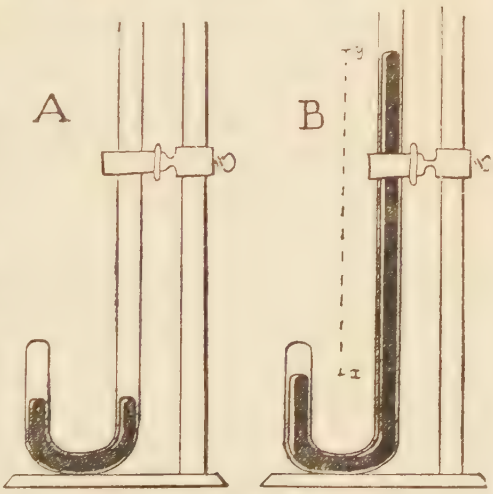


FIG. 42

Fasten the tube in a vertical position, and into it put an inch or two of mercury. Incline the tube to allow a bubble or two of air to escape from the short limb, and adjust the quantity of mercury until its level is the same in both limbs. The air in the short limb will now be at the pressure of the atmosphere. Why?

The pressure of the air is equal to the pressure exerted by a column of mercury about 30 inches or 760 mm. high.

Now measure carefully the length of the column of air in the short limb.

Next pour mercury through a funnel into the long limb until the level of the mercury in it is about 10 inches above that of the mercury in the short limb. Again measure the length of the column of air and measure also the difference in level, *X Y*, of the two columns of mercury, Fig. 42 **B**. Add a few more inches of mercury and take similar measurements. Repeat until the length of the column of air in the short limb is exactly half the original length. Measure *X Y* again.

Now read the barometer to find out the exact pressure of the atmosphere at the end of the experiment. Is the final difference of level, *X Y*, the same as the length of the column of mercury supported by the atmosphere ?

Tabulate your results in the manner shown below.

Pressure of the atmosphere at the time of the experiment = 740 mm.

Number of reading	Length of air column	Length of *X Y*	Total pressure on the air column	Total pressure × length of air column
3	80 mm.	390 mm.	740+390 mm.	1130×80=90,400
4	70 mm.	550 mm.	740+550 mm.	1290×70=90,300

The total pressure on the air column in the short tube will be equal to the height of the column *X Y* plus the height of the mercury barometer at the time of the experiment.

CHARLES' LAW

Exp. 59 has shown you that different gases expand by the same fraction of their volume at 0° C., when their temperature is raised by the same amount. This is Charles' Law.

Charles' Law—*When the pressure is kept constant, all gases expand by $\frac{1}{273}$ of their volume at 0° C. for each degree rise in temperature.*

Note carefully the expression "$\frac{1}{273}$ of their *volume at* 0° *C.*"

Thus 273 c.c. of a gas at 0° C. become 274 c.c. at 1° C.
„ 273 „ „ 283 c.c. at 10° C.
„ 273 „ „ (273+t) c.c. at t° C.
„ 273 „ „ 272 c.c. at −1° C.

Thus 273 c.c. of a gas at 0° C. become 263 c.c. at −10° C.
„ 273 „ „ (273−t)c.c. at −t° C.

It would seem, therefore, that if a gas contracted uniformly, its volume would become nothing at −273° C.; that is, all gases would be liquid at that temperature.

This temperature, −273° C., has never been reached. The lowest temperature hitherto reached is approximately −270° C., obtained by means of the evaporation of helium.

No one, therefore, has ever been able to observe the contraction of a gas down to −273 °C. −273° C., however, serves excellently as a temperature to which to refer all other temperatures. It is known as **absolute zero.** Temperatures referred to absolute zero are known as **absolute temperatures.** T is written after absolute temperatures to show that they are measured on the absolute scale.

Thus 0° C. is 273° T, and 100° C. is 373° T.

If we apply this scale to the volume of gases at various temperatures, we get—

Centigrade Temperature	Absolute Temperature	Volume of Gas
−272° C.	1° T	1
−10° C.	263° T	263
0° C.	273° T	273
10° C.	283° T	283
t° C.	(273+t)° T	273+t

This table shows clearly that the volume of a gas is proportional to its absolute temperature.

Charles' Law may therefore be stated—

When the pressure is constant, the volume of a gas is proportional to its absolute temperature.

Let us now apply our knowledge to the calculation of the volume of gases at various temperatures, when we know the volume at other temperatures.

Example—A gas has a volume of 500 c.c. at 11° C. What is its volume at 0° C.?

0° C. is 273° T, and 11° C. is 284 T.
∴ 284 c.c. of a gas at 11° become 273 c.c. at 0° C.

∴ 1 „ „ 11° becomes $\frac{273}{284}$ c.c. at 0° C.

∴ 500 „ „ 11° become $\frac{273}{284}\times\frac{500}{1}$ c.c. at 0° C.

$=480.6$ c.c. at 0° C.

Example—A gas has a volume of 200 c.c. at 0° C. Calculate its volume at 120° C.

0° C. is 273° T, and 120° C. is $(273+120)°$ T $=393°$ T.

$\therefore$ 273 c.c. of a gas at 0° C. become $(273+120)$ c.c. at 120° C.

$\therefore$ 1 ,, ,, 0° C. becomes $\frac{(273+120)}{273}$ c.c. at 120° C.

$\therefore$ 200 ,, ,, 0° C. become $\frac{(273+120)}{273} \times \frac{200}{1}$ c.c. at 120° C.

$=$ **287.9 c.c. at 120° C.**

Example—A gas has a volume of 150 c.c. at $-12°$ C. What is its volume at 30° C.?

$-12°$ C. is $(273-12)°$ T, and 30° C. is $(273+30)°$ T.

$\therefore$ $(273-12)$ c.c. of a gas at $-12°$ C. become $(273+30)$ c.c. at 30° C.

$\therefore$ 1 ,, ,, $-12°$ C. becomes $\frac{273+30}{273-12}$ c.c. at 30° C.

$\therefore$ 150 ,, ,, $-12°$ C. become $\frac{273+30}{273-12} \times \frac{150}{1}$ c.c. at 30°C.

$=$ **174.1 c.c. at 30° C.**

BOYLE'S LAW

Experiments with the Boyle's Law apparatus have shown you that, when the column XY, Fig. 42, is exactly equal in length to the height of the column of mercury supported by the pressure of the air, the volume of air in the short limb is half the volume it occupied when the mercury was level in both limbs. The pressure on the air in the tube must then be twice the ordinary pressure of the air. The total pressure on the air multiplied by the volume of the air was always the same, or almost the same. This means that the volume of the air diminished in exactly the same proportion as the pressure on the air increased. In order that this may continue to be the case, the volume must be $\frac{1}{3}$ if the pressure is trebled, and $\frac{1}{20}$ of the original volume if the pressure is increased 20 times. Numerous experiments with gases which are not readily converted into liquids have proved that this is the case for all such gases.

Let p be the pressure and v the volume of the gas.

Then v varies as $\frac{1}{p}$ and $pv =$ constant.

This means that the volume of a gas is inversely propor-

tional to the pressure on the gas, and that the product of the pressure and the volume of a gas is always the same for a fixed quantity of gas. These facts are expressed by Boyle's Law.

Boyle's Law—*When the temperature is constant, the volume of a gas varies inversely as the pressure.*

When, therefore, we speak of a certain volume of a gas, we ought to state the pressure on the gas, and, since the volume of a gas changes with temperature, the temperature should also be stated. A standard of pressure must be chosen. The average pressure of the atmosphere is a convenient standard. The pressure of a column of mercury 760 millimetres long is nearly equal to the average pressure of the air, and is therefore chosen as the standard of pressure.

Example—What is the change in the volume of a gas occupying 400 c.c. when the pressure is increased from 740 mm. to 760 mm., the temperature being unchanged?

We know that pressure × volume is a constant.
If p is the old pressure and p^1 the new pressure, and
,, v ,, volume and v^1 ,, volume,
then $\mathbf{pv = p^1v^1}$.
In the above example $p=740$, $v=400$, $p^1=760$, $v^1=?$

$$\therefore 740 \times 400 = 760 \times v^1$$

$$\therefore v^1 = 400 \times \frac{740}{760} = \mathbf{389.4\ c.c.}$$

Therefore the volume of the gas at 760 mm. pressure is 389.4 c.c.

Example—Find the change in volume of 300 c.c. of air when the pressure decreases from 780 to 760, the temperature being unchanged.

$pv=p^1v^1$, $p=780$, $v=300$, $p^1=760$, $v^1=?$

$$\therefore 780 \times 300 = 760 \times v^1$$

$$\therefore v^1 = 300 \times \frac{780}{760} = \mathbf{307.9\ c.c.}$$

From these examples it is obvious that, to find the volume of a gas at various pressures, it is only necessary to multiply by a factor. If the pressure is increased, the volume must be diminished, and we multiply by $\frac{\text{small pressure}}{\text{large pressure}}$.

If the pressure is decreased, the volume must increase, and we multiply by $\frac{\text{large pressure}}{\text{small pressure}}$.

Corrections for temperature and pressure

It is frequently necessary in the laboratory to find the volume of a gas at standard or normal temperature and pressure, that is, at 0° C. and 760 mm. The gas is generally measured at the ordinary temperature of the laboratory, and at the atmospheric pressure at the time of the experiment. The volume of the gas must then be corrected for both temperature and pressure.

The following examples show how this is done.

Example—Find the volume at normal temperature and pressure of 600 c.c. of hydrogen measured at 11° C. and 740 mm. pressure.

Correct first for pressure. The pressure is increased from 740 to 760 mm.

$$\therefore v^1 = 600 \times \frac{740}{760} = \text{volume of gas at } 11^\circ \text{ C. and } 760 \text{ mm.}$$

Now this gas must be cooled from 11° C. to 0° C.

∴ Volume of gas at 0° C. and 760 mm. pressure

$$= 600 \times \frac{740}{760} \times \frac{273+0}{273+11} = \mathbf{561.6 \text{ c.c.}}$$

Example—A gas occupies a volume of 250 c.c. The temperature of the laboratory is 15° C., and the atmospheric pressure is 767 mm. Find the volume of the gas at normal temperature and pressure.

$$\text{Volume of gas at } 0^\circ \text{ C. and } 760 \text{ mm.} = 250 \times \frac{767}{760} \times \frac{273+0}{273+15}$$

$$= \mathbf{239.2 \text{ c.c.}}$$

Very frequently a gas is collected, levelled,* and measured over water. The gas is saturated with water vapour. The water vapour exerts a pressure which has a fixed value for definite temperatures. (See Appendix II). The pressure due to the gas itself, together with the water vapour pressure, is equal to the pressure of the atmosphere. Therefore the pressure due to the gas is equal to the atmospheric pressure minus the water vapour pressure. The correction for water vapour pressure makes a considerable difference in the volume of gas.

Example—56 c.c. of oxygen were collected over water. The temperature was 19° C., and the height of the barometer

* Levelling consists of bringing the liquid inside and outside the tube to the same level.

720 mm. Find the volume of the dry gas at 0° C. and 760 mm.

Pressure due to aqueous vapour at 19° C. = 16.4 mm.
∴ True pressure of oxygen = 720 − 16.4 = 703.6 mm.
∴ Volume of dry oxygen at 0° C. and 760 mm.

$$= 56 \times \frac{703.6}{760} \times \frac{273 - 0}{273 + 19}$$
$$= 48.5 \text{ c.c.}$$

CHAPTER VIII

FUNDAMENTAL LAWS OF CHEMISTRY — EQUIVALENT WEIGHTS ATOMIC THEORY—CHEMICAL SYMBOLS—CALCULATIONS INVOLVING THE USE OF CHEMICAL EQUATIONS, ETC.

Exp. 61—To make copper oxide in several ways and find out if it always contains the same weight of copper

Required—Copper hydroxide, copper carbonate, copper nitrate; pieces of copper foil for making boats; small evaporating basin, hard glass tubes, corks, balance

Directions—Heat strongly a few grams of (1) copper

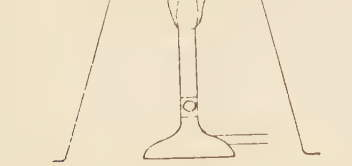


FIG. 43

hydroxide, (2) copper carbonate, (3) copper nitrate in a small dish. Copper oxide is obtained in each case. Allow to cool.

Bend a piece of copper foil into the shape of a boat. Weigh the boat. Into it put one or two grams of your copper oxide and weigh again. Fit up the tube as in Fig. 43. Pass a gentle stream of coal gas for a minute, light the issuing gas,

and heat the copper oxide at first gently and then strongly. When all the black oxide is completely converted to copper, take away the flame and allow to cool in a slow stream of coal gas. Why? Weigh the boat again.

The coal gas has taken out the oxygen from the copper oxide. Repeat with the other specimens of copper oxide you have made. Calculate the percentage of copper in each specimen. Better results are obtained if hydrogen is used instead of coal gas.

Exp. 62—To find the weight of magnesium oxide obtained by burning magnesium in air

Required—Crucible and lid, magnesium ribbon, balance, pipe-clay triangle

Directions—Dry and weigh a small crucible and lid. Clean about two feet of magnesium ribbon with emery paper, bend it as shown in Fig. 44, put it into the crucible, and weigh again. Heat the crucible on the triangle, raise the lid with a glass rod, light the magnesium with the bunsen flame and replace the lid. Continue to heat the crucible, and slightly raise the lid from time to time. When the burning is nearly finished, heat strongly with the lid off for a minute or two. Replace the lid, allow to cool; weigh again.

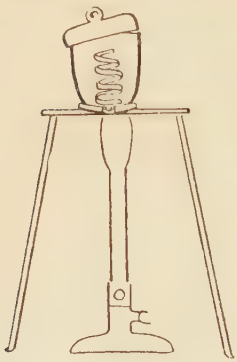


FIG. 44

If the experiment has been carefully performed, very few fumes of magnesium oxide will have escaped.

Calculate the percentage of magnesium and oxygen in magnesium oxide.

Exp. 63—To find if magnesium oxide prepared by heating magnesium nitrate contains the same percentage of oxygen as the oxide obtained by burning magnesium

Required—Magnesium, nitric acid, crucible and lid, balance

Directions—Weigh a dry crucible and lid. Weigh into the crucible about .3 gram of magnesium ribbon. Place the lid on the crucible so that a small opening is left. Using a glass tube drawn out to a jet, add nitric acid, diluted with its own

volume of water, a drop or two at a time, until no metallic magnesium remains. Evaporate the liquid very slowly to dryness with a small flame placed about nine inches below the crucible, taking great care that no liquid escapes over the side of the crucible. When all liquid has been evaporated, heat the crucible strongly for several minutes; re-heat and re-weigh until two consecutive weighings are the same.

The magnesium has been converted, first, into magnesium nitrate, and then into magnesium oxide. Calculate the percentage of magnesium and oxygen in the magnesium oxide and compare your result with that obtained in Exp. 62.

LAW OF CONSTANT PROPORTIONS

Your experiments, if accurately carried out, should have proved that copper oxide and magnesium oxide, made by different methods, contain always the same proportions of oxygen and metal. *It has been found by Stas and other chemists that a chemical compound, however it is prepared, always contains the same elements in the same proportions.* This is usually called the **Law of Constant Proportions** or the **Law of Definite Proportions.** It may be stated: *Every chemical compound has a definite composition.*

The evidence upon which the law rests is founded on a great number of researches in which chemical compounds have been made and analysed. Every known chemical compound confirms to the law.

You have found in your earlier work that the same amount of hydrogen was always displaced by equal weights of zinc, that the same weight of oxygen was always present in potassium chlorate, and that the same weight of carbon dioxide was always contained in calcium carbonate. Here is evidence which you have yourself obtained of the truth of the law. If you were never sure of obtaining the same weight of carbon dioxide from 100 grams of pure calcium carbonate, you would have been justified in regarding the law as untrue, or in thinking that calcium carbonate was not a chemical compound. Of course your experiments must be quite accurate, otherwise it is impossible to draw any conclusion

CHEMICAL EQUIVALENTS

It is necessary for chemists to have some standard with

which to compare the amounts of substances which combine together. Hydrogen is the lightest substance known, and is therefore a very convenient standard for comparison. The term used for the weight of an element which will combine with or replace one unit weight of hydrogen is **equivalent weight.** The equivalent weight of hydrogen is therefore taken as 1.

Unfortunately hydrogen cannot combine with, or be replaced by, every element in a manner suitable for accurate measurement. The equivalent weights of many elements must therefore either remain undetermined, or be found by other means. Suppose that an element X does not combine with or replace hydrogen, and that its equivalent weight has to be determined. It should be possible to find the equivalent weight of an element Z, which does replace or combine with hydrogen, and then find the amount of the element X which combines with or replaces the equivalent weight of the element Z. This amount of X will be its equivalent weight. Oxygen combines with nearly every element. If we can find the equivalent weight of oxygen accurately we shall therefore be able to find the equivalent weight of elements which combine with oxygen.

Exp. 64—To find the equivalent weight of oxygen

Required—Hard glass tube, hydrogen apparatus with drying tube, granular copper oxide, calcium chloride tube, balance

Directions—Fit up the apparatus shown in Fig. 45.

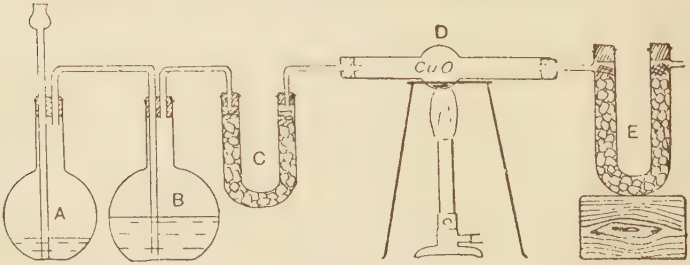


FIG. 45

A = Hydrogen apparatus.

B = Potassium permanganate solution to purify hydrogen.

C = Calcium chloride tube to dry the hydrogen.
D = Hard glass tube fitted with india-rubber corks.
E = Calcium chloride tube to collect the water formed.

Weigh the clean, dry, hard glass tube. Into it put about 10 grams of granular copper oxide and weigh again. Weigh the calcium chloride tube **E**. Pass a slow stream of hydrogen for some minutes, and then heat the copper oxide. The hydrogen reduces the copper oxide to copper, and the water formed is collected by the calcium chloride tube **E**. Drive out any water which may condense in **D**, or the tubes leading from it, by very gently warming. Take care that you do not heat the india-rubber corks.

After twenty minutes remove the flame and allow the apparatus to cool in the stream of hydrogen.

Weigh **D** and **E** again.

Calculate the weight of oxygen which has combined with 1 gram of hydrogen.

Exp. 65—To find the equivalent weight of a metal by replacement of hydrogen

Required—Burette and stand, or funnel, 150 c.c. flask, trough and measuring tube, metals, acids, copper gauze

Directions—Fit up the apparatus shown in Fig. 46.

A = Burette. This may be replaced by a funnel fitted with tubing and a clip.

B = Flask containing metal wrapped in copper wire gauze.

C = 100 c.c. measuring tube.

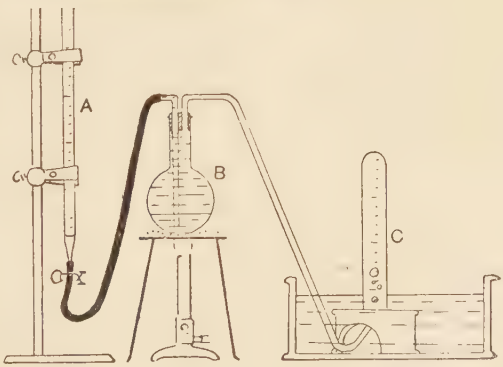


FIG. 46

Weigh out accurately about .08 gram of magnesium ribbon, fold it up, and wrap it in a small piece of copper gauze. [The copper gauze is not acted upon by hydrochloric acid, and prevents the escape,

towards the end of the experiment, of small pieces of magnesium through the delivery tube.] Introduce the metal and gauze into the flask. See that the end of the delivery tube is exactly level with the bottom of the cork. Why? Fill the flask and tubes completely with water by running in water from the burette. Next fill the burette with strong hydrochloric acid. Put the measuring tube over the end of the delivery tube and run in acid from the burette until the hydrogen comes off freely.

When hydrogen no longer comes off, run in more acid to make sure that enough acid has been added. When the hydrogen has undoubtedly ceased to come off, drive out the hydrogen in the flask and tubes by means of a rapid stream of water from the burette.

Take out the measuring tube by means of a small dish and level in a tall vessel full of water to make the pressure inside equal to atmospheric pressure. Read the barometer, take the temperature of the water in the tall vessel and correct the volume of hydrogen for temperature and pressure, allowing for the pressure of water vapour, as shown on pages 80 and 81.

Calculate the weight of the hydrogen displaced and the equivalent weight of magnesium, *i.e.* the weight of magnesium which would displace 1 gram of hydrogen.

A litre of hydrogen measured at 0° C. and 760 mm. pressure weighs .09 gram.

This method may also be used for aluminium, iron, and zinc. The weights used should be about .07 gram for aluminium, .02 gram for iron, and .2 gram for zinc.

For tin and cadmium the method may be used with the following modifications. Use about .2 gram of tin and about .4 gram of cadmium.

(1) The air dissolved in the hydrochloric acid and water used in the experiment must be got rid of by boiling each for at least ten minutes. Why?

(2) The flask **B** must be heated.

(3) A few drops of a solution of platinic chloride should be added to the strong hydrochloric acid before it is used. This causes a deposition of platinum on the tin or cadmium, with the result that the tin or cadmium dissolves much more rapidly.

Exp. 66—To find the equivalent of a metal by formation of the oxide of the metal

Required—Crucible and lid, metals in foil or granulated, strong nitric acid, glass tubing drawn out to a jet, triangle

Directions—Weigh a clean dry crucible and lid and into the crucible weigh from .5 to 1 gram of the metal. Displace the lid slightly, and by means of a tube drawn out to a jet, add strong nitric acid, *drop by drop*, and wait after the addition of each drop until action has ceased. In the case of copper and some other metals the addition of two or three drops of water will cause the action to take place more readily.

Place the crucible on a triangle at a height of about a foot above a very small flame and continue to add nitric acid, a drop at a time, as long as any metal remains unchanged. When all the liquid has been evaporated, gradually lower the crucible until it is in contact with the small flame. Remove the flame, allow to cool, and again add a few drops of nitric acid. Heat again with the flame a foot below the crucible until all the acid has evaporated. Finally gradually raise the temperature to full redness for ten minutes. Cool and weigh.

Again add a few drops of nitric acid, evaporate, heat to redness, cool and re-weigh. This must be repeated until two consecutive weighings are the same. The metal is then completely converted to oxide.

Calculate the weight of the metal which corresponds to 8 grams of oxygen. This is the equivalent weight of the metal.

This method may be used for antimony, bismuth, copper, lead, magnesium, tin, and zinc.

Exp. 67—To find the weight of one metal displaced by an equivalent weight of another metal

Required—Evaporating dish, solution of copper sulphate, zinc foil, short glass rod, alcohol, ether balance

Directions—Weigh an evaporating dish, and into it weigh from .5 to 1 gram of zinc foil which has been cleaned with emery paper. Half fill the dish with copper sulphate solution and stir with a short glass rod. Do not remove the rod from the liquid. Why? If the colour of the copper sulphate entirely disappears, add more copper sulphate solution and

continue until no more zinc can be seen or felt with the glass rod.

Let the copper settle, and very carefully pour off the liquid from the metal as completely as possible without loss of copper. Add water, stir, allow to settle, and again pour off. Repeat several times. Now wash two or three times with alcohol. Wash off copper from the rod, drain the alcohol from the copper, wash twice with ether, and dry the dish and its contents in the steam oven or by very gentle heating on a sand bath. The copper is easily converted to oxide and therefore must not be made very hot. Weigh the dish.

Calculate the amount of copper which would be precipitated by 32.5 grams of zinc. 32.5 is the equivalent weight of zinc.

Repeat the experiments, using .1 gram of clean magnesium ribbon and a strong solution of silver nitrate. Find the amount of silver replaced by 12 grams of magnesium.

Note—Do not waste silver solution or metallic silver. Put them into the silver residue bottle.

Exp. 68—To find the weight of chlorine which combines with an equivalent weight of silver

Required—Hydrogen apparatus, hard glass tube, porcelain boat, silver chlorine

Directions—Weigh the boat. Into it introduce about .5 gram of silver chloride and weigh again. Put the boat into the tube, pass hydrogen for a minute or two, and then heat strongly in a current of hydrogen until the chloride is completely converted to silver. Hydrochloric acid comes off and silver is left. Allow to cool. Weigh.

Silver chloride consists of silver and chlorine only, so that the loss of weight represents the weight of chlorine, which was combined with the weight of silver left in the boat at the end of the experiment.

Calculate the weight of chlorine which combines with 108 grams of silver.

CHEMICAL EQUIVALENTS OR COMBINING WEIGHTS (*continued*)—

The equivalent weight of oxygen you have found to be very nearly 8. Very accurate determinations of the equivalent by

the most eminent chemists have shown that it is 7.94. For your experiments the number 8 will be sufficiently accurate.

From your own experiments and those of others of your class you should now be able to construct a table of equivalents of many of the metals and of some non-metals. Make such a table and compare it with the following: Hydrogen = 1, Oxygen = 8, Magnesium = 12, Zinc = 32.5, Tin = 29.5, Copper = 31.5, Lead = 103.5, Iron = 28, Aluminium = 9, Antimony = 40, Bismuth = 68.8, Cadmium = 56, Silver = 108, Chlorine = 35.5.

Compare the equivalent weights of magnesium, zinc, and tin obtained by replacement of hydrogen and by combination with oxygen. Both methods will be found to have given the same equivalent weight for these metals. It was therefore justifiable to think that the weights of metals combining with 8 grams of oxygen were the weights of those metals which would displace 1 gram of hydrogen. In the case of all the equivalent weights determined by means of oxygen in the above manner, it has been found that these weights are the weights which will displace 1 gram of the hydrogen of acids to form salts.

Again, you should have found that the equivalent weight of magnesium, 12 parts, will replace 108 parts of silver; 108 should therefore be the equivalent weight of silver. Silver does not combine with hydrogen or displace it in the way that zinc displaces hydrogen. Magnesium can, however, easily be made to take the place of hydrogen in acids.

It is found that 12 grams of magnesium replace 1 gram of hydrogen. Therefore the weight of silver, 108, displaced by 12 of magnesium, is the equivalent weight of silver.

Again, 108 grams of silver combine with 35.5 grams of chlorine. Therefore 35.5 should be the equivalent weight of chlorine. In hydrochloric acid, as we shall see later, 1 gram of hydrogen is combined with 35.5 grams of chlorine. Therefore 35.5 is the equivalent weight of chlorine.

We can then define **equivalent weight** *as the weight of an element which will combine with, replace, or play the same part as* 1 *part by weight of hydrogen or* 8 *parts by weight of oxygen.*

Calculate the equivalent weights of copper and magnesium from the results you obtained in Exp. 61 and Exp. 62.

Exp. 69—To reduce the red oxide of copper (cuprous oxide) to metal, to calculate from the result the equivalent of copper, and to compare this equivalent with that obtained by reduction of the black oxide (cupric oxide)

Required—Hard glass tube fitted as in Exp. 61, *cuprous oxide, cupric oxide, balance, thin copper sheet*

Directions—Weigh the copper boat; introduce into the boat one or two grams of cuprous oxide. Weigh again. Reduce the oxide to metal by heating in a stream of coal gas. Allow to cool in the coal gas. Weigh the boat again.

If hydrogen is used instead of coal gas, better results are obtained.

Calculate the weight of copper which was combined with 8 grams of oxygen.

Compare the equivalent obtained with that you found from Exp. 66. If you have not done Exp. 66 satisfactorily, reduce cupric oxide in the same way as you reduced cuprous oxide, and calculate the equivalent of copper from the result.

Exp. 70—To reduce oxides of lead by heating them in coal gas, and to compare the equivalents of lead calculated from the results

Required—The same apparatus as in Exp. 69; *lead monoxide, red lead, and red peroxide; thin copper sheet*

Directions—Weigh the copper boat. Into the boat weigh 2 or 3 grams of one of the oxides of lead. Reduce to metal by heating in coal gas or hydrogen. Re-weigh the boat and calculate the equivalent of lead.

Repeat the experiment with the other oxides of lead.

Is there any relationship between the equivalents you have obtained?

Note—If a muffle furnace is available, good results can be obtained by reducing 3 or 4 grams of the oxide in a charcoal crucible and weighing the button of metallic lead produced.

LAWS OF MULTIPLE PROPORTIONS AND RECIPROCAL PROPORTIONS

Exps. 69 and 70 have shown you that one metal may have more than one equivalent weight. In other words, you

have found that the proportions of oxygen and metal in the oxides of copper and lead are not always the same. Is not this a direct contradiction of the law of constant proportions? It is not; for each one of the oxides used always contains exactly the same proportions of metal and of oxygen.

Possibly your results, and even the average result of the class, may not have been accurate enough to show any clear relation between the equivalents obtained.

The following are accurate results:—

	Cuprous Oxide	*Cupric Oxide*
Copper	63	31.5
Oxygen	8	8

	Lead Monoxide	*Red Lead*	*Lead Peroxide*
Lead	103.5	77.62	51.75
Oxygen	8	8	8

The equivalents of copper are in the ratio $\frac{63}{31.5} = \frac{2}{1}$.

The equivalents of lead are in the ratio 103.5 : 77.62 : 51.75
that is 4 : 3 : 2

Many other elements combine together in more than one proportion. For instance, marsh gas contains 1 gram of hydrogen combined with 3 grams of carbon, and ethylene contains 1 gram of hydrogen combined with 6 grams of carbon.

Nitrogen forms five compounds with oxygen.

Nitrous oxide contains 28 grams of nitrogen combined with 16 grams of oxygen.

Nitric oxide contains 28 grams of nitrogen combined with 32 grams of oxygen.

Nitrogen trioxide contains 28 grams of nitrogen combined with 48 grams of oxygen.

Nitrogen peroxide contains 28 grams of nitrogen combined with 64 grams of oxygen.

Nitrogen pentoxide contains 28 grams of nitrogen combined with 80 grams of oxygen.

The ratio of the amounts of oxygen is here 1 : 2 : 3 : 4 : 5.

The results of the analyses of many similar cases can be expressed in a simple law called the **Law of Multiple Proportions.** *When two elements, A and B, form more than one*

compound with one another, the weights of A which combine with a fixed weight of B bear a simple relation to one another. Thus, in the case of the oxides of nitrogen, the fixed weight of B is 28 grams of nitrogen. With this combine 16, 32, 48, 64, 80 grams of oxygen to give the different oxides. These weights are the weights of A, and the relation between them is simple, viz. 1 : 2 : 3 : 4 : 5. In the case of the oxides of lead, the fixed weight was 8 grams of oxygen. The weights of lead combined with this were in the ratio 2 : 3 : 4, again a simple relation.

You have found out that 8 grams of oxygen combine with 1 gram of hydrogen ; that 12 grams of magnesium combine with 8 grams of oxygen ; that 108 grams of silver replace 12 grams of magnesium ; and that 108 grams of silver combine with 35.5 grams of chlorine. All these quantities are equivalent to one another. Now, hydrogen, oxygen, and magnesium will all combine with chlorine. The question arises as to whether the equivalents of hydrogen, oxygen, and magnesium are the quantities of these elements which combine with the equivalent of chlorine.

Analyses of compounds give the following results :—

Chlorine Monoxide		*Chlorine Peroxide*		*Hydrochloric Acid*		*Magnesium Chloride*	
Chlorine	35.5	35.5		Chlorine	35.5	Chlorine	35.5
Oxygen	8	32		Hydrogen	1	Magnesium	12

The equivalent weight of chlorine, therefore, combines with the equivalent weights of hydrogen and magnesium and with that of oxygen in the case of chlorine monoxide. In the case of chlorine peroxide it will be noticed that the equivalent weight of chlorine combines with four times the equivalent weight of oxygen.

Again, lead has been found to have three equivalent weights, 103.5, 77.62, and 51.75. Lead forms a compound with chlorine. Which, if any, of these equivalent weights is the weight which combines with 35.5 of chlorine ? Analysis of lead chloride gives—chlorine = 35.5 ; lead = 103.5.

Results obtained from examinations of many other compounds have given rise to another law known as the **Law of Reciprocal Proportions.** The law may be stated : *If elements A, B, C, D, etc., combine with another element X, then the quantities of A, B, C, D, etc., which combine with X are also*

the quantities, or simple multiple of the quantities, in which A, B, C, D, etc., combine with one another.

The examples taken are expressed diagrammatically in Fig. 47.

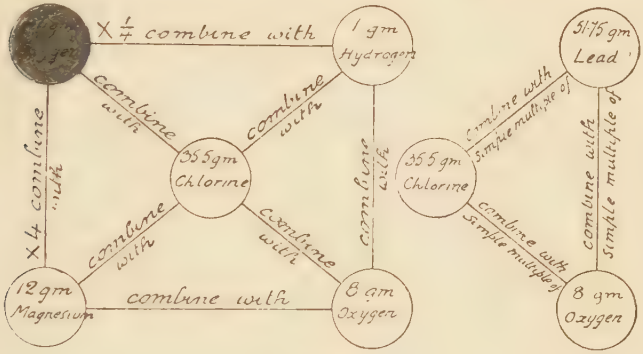


FIG. 47

GAY LUSSAC'S LAW OF VOLUMES

We have seen that the weights of elements which combine together follow fixed laws. Let us now consider the volumes of gases combining together. Do these volumes also obey any law?

Some of the facts you have already come across.

Two volumes of hydrogen combine with 1 volume of oxygen to form water. One volume of hydrogen combines with 1 volume of chlorine to form hydrochloric acid. If the water is kept in a gaseous state, that is, if the oxygen and hydrogen are made to combine at a temperature above 100° C., the volume of the steam formed is found to be 2 volumes. Similarly, 1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrochloric acid gas.

Carbon combines with 2 volumes of oxygen to give 2 volumes of carbon dioxide. Sulphur combines with 2 volumes of oxygen to give 2 volumes of sulphur dioxide.

All other gases combine in similar simple volumes. Gases, in fact, obey **Gay Lussac's Law of Volumes,** which states that *the volumes of gases combining together bear a simple relation*

to one another and to the volume of the resulting product, if gaseous.

In the case of hydrogen and oxygen giving steam, the relation is 2 : 1 : 2.

In the case of hydrogen and chlorine giving hydrochloric acid, the relation is 1 : 1 : 2.

AVOGADRO'S LAW

Let us now look for an explanation of these simple relations.

You have seen that the weight of a litre of hydrogen, or any other gas, can readily be found, Exp. 58. If the weight of a litre of oxygen is compared with that of a litre of hydrogen, it is found to be 16 times as great. A litre of chlorine is found to weigh 35.5 times as much as a litre of hydrogen. The number 16 is twice the equivalent weight of oxygen, and 35.5 is the equivalent weight of chlorine. It would seem, therefore, that there is some relation between the density of a gaseous element compared with hydrogen and the equivalent weight of the element.

Again, Boyle's Law and Charles' Law show that all gases behave in the same way under changes of temperature and pressure. How can we account for the fact that gases as different in properties as chlorine, hydrogen, oxygen, carbon dioxide, etc., behave in the same way ? There must be something in common between all these gases. A consideration of their properties will show that they do not possess one ordinary property in common, other than their similar behaviour towards temperature and pressure. An Italian physicist, Avogadro, in 1811, suggested an explanation, namely, that all gases contained equal numbers of particles in equal volumes.

Now if equal numbers of particles are present in equal volumes of gases, it is exceedingly likely that those gases, however different they may be in ordinary properties, will behave similarly under changes of temperature and pressure.

Is this suggestion also in accordance with Gay Lussac's law ? If equal volumes of gases are brought together, equal numbers of particles of these gases are brought together, according to Avogadro. When 1 volume of hydrogen combines with 1 volume of chlorine it gives 2 volumes of hydrochloric acid.

Therefore, according to Avogadro, x particles of hydrogen combine with x particles of chlorine to give $2x$ particles of hydrochloric acid. Each particle of hydrochloric acid must contain at least 1 particle of hydrogen or it would not be hydrochloric acid.

Therefore there must be at least $2x$ particles of hydrogen in the hydrochloric acid. There were, however, only x particles of hydrogen at the start, and matter cannot be created. Something must be wrong.

Avogadro saw this discrepancy and modified his theory. He suggested that there are two kinds of particles: (1) atoms, the smallest particles of an element which can exist at all; (2) molecules, consisting of two or more atoms, and capable of existing alone.

Let us now suppose that each particle or molecule of hydrogen or chlorine contains 2 atoms. Then x molecules of

FIG. 48

hydrogen contain $2x$ atoms of hydrogen, and $2x$ molecules of hydrochloric acid also contain $2x$ atoms of hydrogen. The discrepancy has disappeared. This is expressed diagrammatically in Fig. 48.

Avogadro's suggestion, or *hypothesis*, has been found to be in accordance with all the facts.

Avogadro's Law—*Under the same conditions of temperature and pressure, equal volumes of gases contain equal numbers of molecules.*

"Molecule" and "Atom" may be defined as follows:—

Molecule *is the smallest part of an element or compound which can exist alone and possess the properties of that element or compound.*

Atom *is the smallest part of an element which can take part in a chemical change.*

It used to be considered that atoms were indivisible. This is not true, for, in the last few years, atoms of some element

have been found to give off much smaller bodies called "electrons." These electrons, however, do not take part independently in chemical change, as far as is yet known.

ATOMIC THEORY

The idea of atoms and molecules is of the greatest importance to chemists, for on what is known as the Atomic Theory is built up the huge structure of modern chemistry.

Dalton, a Manchester schoolmaster, was the founder of the atomic theory. At the beginning of the nineteenth century Dalton suggested that chemical combination, and chemical action generally, took place between atoms of substances, *i.e.* that simple numbers of atoms of fixed weight combined together. He attempted, with some success, to fix the relative weights of these atoms. He founded his suggestion on the laws of definite and multiple proportions.

These laws, together with Gay Lussac's law of volumes and the law of reciprocal proportions, evidently point to chemical action taking place between fixed masses of substances. For instance, 31.5 grams of copper combine with 8 grams of oxygen or 35.5 grams of chlorine; 8 grams of oxygen combine with 32.5 grams of zinc; 32.5 grams of zinc combine with 35.5 grams of chlorine.

Equivalent weights such as these must be closely connected with the weights of the atoms. They need not be the same as the weights of the atoms, because an atom of one element might combine with more than one atom of another element. Thus, 1 atom of oxygen might combine with 2 atoms of hydrogen. If the atom of hydrogen weighs 1 and the atom of oxygen 16, then 16 grams of oxygen will combine with 2 grams of hydrogen. The equivalent of oxygen will be 8. This we know to be the case.

Chemists have, by a number of methods, succeeded in finding the comparative weights of the atoms and molecules of elements and compounds. The standard of atomic weight and molecular weight is the weight of 1 atom of hydrogen. The atomic weight of hydrogen is therefore taken as 1.

The **Atomic Weight** *of an element is the ratio of the weight of an atom of the element to the weight of an atom of hydrogen.*

Many atoms seem to have a power of combining with, and attaching themselves to, other atoms to form the complex

particles called molecules. To the chemical attraction of atom for atom the name **chemical affinity** is given. What chemical affinity is, no one knows with any certainty. Why an atom should have an affinity for an atom of one substance and no affinity for an atom of another substance is also not properly understood.

Atoms and molecules are exceedingly minute. Lord Kelvin has calculated that if a drop of water could be magnified to the size of the earth, the molecules in it would appear to be larger than small shot but smaller than cricket balls.

The atoms of one element have equal weights. Thus, one atom of chlorine has the same weight as any other atom of chlorine; an atom of oxygen has the same weight as any other atom of oxygen; but an atom of oxygen has a weight different from that of an atom of chlorine or any other element. Similarly the molecules of any particular element or compound have each the same weight, but generally a weight different from that of the molecule of any other element or compound. Two different compounds may, however, have the same molecular weight.

CHEMICAL SYMBOLS AND EQUATIONS

The atoms and molecules of chemical substances are represented by means of symbols and formulæ. The symbol chosen is often the initial letter of the English or Latin name of the element. When several elements have the same initial letter, for one of them the initial is used, for the others a combination of the initial and another letter of the name.

Element	*Symbol*	*Element*	*Symbol*
Hydrogen	H	Carbon	C
Oxygen	O	Chlorine	Cl
Nitrogen	N	Calcium	Ca
Phosphorus	P	Lead (Plumbum)	Pb
Copper (Cuprum)	Cu	Sodium (Natrium)	Na

These symbols are more than mere shorthand. They express a definite weight, the atomic weight of the element.

Molecules are expressed in the following way:—

H_2 = a molecule of hydrogen containing 2 atoms.

O_2 = a molecule of oxygen containing 2 atoms.

CO_2 = a molecule of carbon dioxide containing 1 atom of carbon and 2 atoms of oxygen.

$KClO_3$ = a molecule of potassium chlorate containing 1 atom of potassium, 1 atom of chlorine, and 3 atoms of oxygen.

$CaCO_3$ = a molecule of calcium carbonate containing 1 atom of calcium, 1 atom of carbon, and 3 atoms of oxygen.

Chemical changes are expressed by means of equations. Matter is indestructible, therefore the same weight of matter is present after a chemical change as before the change. Thus :—

Mercuric Oxide		Mercury		Oxygen
$2HgO$	=	$2Hg$	+	O_2

This means that when 2 molecules of mercuric oxide are heated they give 2 molecules of mercury and 1 molecule of oxygen.

In the equation we see that mercuric oxide consists of 1 atom of mercury and 1 atom of oxygen, that a molecule of mercury contains 1 atom, and that a molecule of oxygen contains 2 atoms.

Calcium Carbonate		Hydrochloric Acid		Calcium Chloride		Carbon Dioxide		Water
$CaCO_3$	+	$2HCl$	=	$CaCl_2$	+	CO_2	+	H_2O

This means that a molecule of calcium carbonate reacts with 2 molecules of hydrochloric acid to give 1 molecule of calcium chloride, 1 molecule of carbon dioxide, and 1 molecule of water. The composition of these molecules is also indicated.

CALCULATIONS INVOLVING THE USE OF CHEMICAL EQUATIONS

The equations tell us not only these facts, but, if we know the atomic weights of the elements present, they tell us also the weights of the substances reacting and the weights of the substances produced.

Thus, the atomic weight of Ca = 40, C = 12, O = 16, Cl = 35.5, H = 1.

$\therefore$ the molecule of $CaCO_3$ weighs $40 + 12 + 3 \times 16 = 100$

,,	,,	HCl	,,	$1 + 35.5$	$= 36.5$
,,	,,	$CaCl_2$	,,	$40 + 2 \times 35.5$	$= 111$
,,	,,	CO_2	,,	$12 + 2 \times 16$	$= 44$
,,	,,	H_2O	,,	$2 \times 1 + 16$	$= 18$

It appears, therefore, from the above equation, that 100 grams of calcium carbonate react with 73 grams of hydrochloric acid, and give 111 grams of calcium chloride, 44 grams of carbon dioxide, and 18 grams of water.

It is evident that, if we know the equation representing a chemical change, we can calculate the weights of substances, reacting and produced.

Example—Calculate the weight of hydrogen that can be obtained from 13 grams of zinc. [Atomic weights: Zn = 65, H = 1.]

Zinc		Hydrochloric Acid		Zinc Chloride		Hydrogen
Zn	+	$2HCl$	=	$ZnCl_2$	+	H_2

The equation shows that 65 grams of zinc give 2 grams of hydrogen.

$\therefore$ 1 gram of zinc gives $\frac{2}{65}$ gram of hydrogen.

$\therefore$ 13 grams of zinc give $\frac{2}{65} \times \frac{13}{1}$ gram of hydrogen.

$= .4$ **gram of hydrogen.**

Example—Calculate the weight of lime which would give 30 grams of calcium carbonate. [Atomic weights: Ca = 40, O = 16, C = 12.]

Lime		Carbon Dioxide		Calcium Carbonate
CaO	+	CO_2	=	$CaCO_3$
$40+16$		$12+32$		$40+12+3\times16$
$=56$		$=44$		$=100$

From the equation we see that—

100 grams of calcium carbonate are obtained from 56 grams of lime.

$\therefore$ 1 gram " " is " $\frac{56}{100}$ gram of lime.

$\therefore$ 30 grams " " are " $\frac{56 \times 30}{100}$ "

= 16.8 grams of lime.

The volumes of gases produced can also be calculated from equations. Avagadro's Law states that equal volumes of gases contain equal numbers of molecules, if the gases are at the same temperature and pressure. That is, a molecule of hydrogen will occupy the same volume as a molecule of any other gas at the same temperature and pressure. If, then, we find the volume occupied by a molecular weight of hydrogen at a standard temperature and pressure, we shall know, once for all, the volume occupied by a molecular weight of any

other gas at that standard temperature and pressure. The standard temperature and pressure chosen are 0° C. and 760 mm. respectively.

It has been shown (see Avogadro's Law) that a molecule of hydrogen must contain at least two atoms. It may, however, contain more than two atoms. That the hydrogen molecule contains only two atoms can readily be proved. We have already learnt that—

1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrochloric acid.

∴ n molecules of hydrogen combine with n molecules of chlorine to form $2n$ molecules of hydrochloric acid (Avogadro's Law).

But $2n$ molecules of hydrochloric acid contain at least $2n$ atoms of hydrogen.

∴ each of the n molecules of hydrogen must contain at least 2 atoms of hydrogen.

Now, if the molecule of hydrochloric acid contained two atoms of hydrogen, it would be possible to replace one atom of hydrogen and make one compound, and afterwards replace the second atom of hydrogen and make a completely different compound. This cannot be done. Therefore a molecule of hydrochloric acid contains only one atom of hydrogen. Consequently the molecule of hydrogen cannot contain more than two atoms of hydrogen.

The volume of 2 grams of hydrogen, *i.e.* of a molecular weight in grams, is nearly 22.24 litres at 0° C. and 760 mm. pressure.

Therefore a molecular weight in grams of any gas at 0° C. and 760 mm. pressure occupies 22.24 litres.

Example—Calculate the volume of hydrogen at 0° C. and 760 mm. pressure that can be obtained from 4.5 grams of water. [Atomic weight: H = 1, O = 16.]

$2H_2O$	=	$2H_2$	+	O_2
$2 \times (2+16)$				
$=36$		2 molecules		one molecule

From equation we see that 36 grams of water give 2 molecular volumes of hydrogen at normal temperature and pressure.

∴ 36 grams of water give 44.48 litres of hydrogen at 0° C. and 760 mm. pressure.

∴ 1 gram of water gives $\frac{44.48}{36}$ litres of hydrogen at 0° C. and 760 mm. pressure.

$\therefore$ 4.5 grams of water give $\frac{44.48 \times 4.5}{36}$ litres of hydrogen at 0° C. and 760 mm. pressure.

= 5.56 litres of hydrogen.

Example—Calculate the volume of hydrochloric acid, measured at 12° C. and 750 mm. pressure, that can be obtained from 58.5 grams of salt. [Atomic weights : Na = 23, Cl = 35.5.]

Salt		Sulphuric Acid		Sodium Sulphate		Hydrochloric Acid
$2NaCl$	+	H_2SO_4	=	Na_2SO_4	+	$2HCl$
$2(23+35.5)$ = 117						2×22.24 litres at 0° C. and 760 mm. pressure.

From equation we see that

117 grams of salt give 44.48 litres of hydrochloric acid at 0° C. and 760 mm. pressure.

$\therefore$ 58.5 grams of salt give $\frac{44.48 \times 58.5}{117}$ litres of hydrochloric acid at 0° C. and 760 mm. pressure.

This volume of hydrochloric acid will occupy at 12° C. and 750 mm. pressure a volume of $\frac{44.48 \times 58.5}{117} \times \frac{760}{750} \times \frac{285}{273}$ litres.

= 23.5 litres.

Example—What weight of potassium chlorate would be necessary to produce 25 litres of oxygen measured at 7° C. and 720 mm. pressure ? [Atomic weights : K = 39, Cl = 35.5, O = 16.]

Potassium Chlorate		Potassium Chloride		Oxygen
$2KClO_3$	=	$2KCl$	+	$3O_2$
$2(39+35.5+3 \times 16)$ = 245				3×22.24 litres at 0° C. and 760 mm. = 66.72 litres

25 litres of oxygen at 7° C. and 720 mm. pressure occupy at 0° C. and 760 mm. pressure a volume of $25 \times \frac{273}{280} \times \frac{720}{760}$ litres.

From equation we see that

66.72 litres of oxygen at 0° C. and 760 mm. are obtained from 245 grams of potassium chlorate.

$\therefore$ 1 litre of oxygen at 0° C. and 760 mm. is obtained from $\frac{245}{66.72}$ grams of potassium chlorate.

$\therefore 25 \times \frac{273}{280} \times \frac{720}{760}$ litres of oxygen at 0° C. and 760 mm. are obtained from $\frac{245}{66.72} \times \frac{25}{1} \times \frac{273}{280} \times \frac{720}{760}$ grams of potassium chlorate.

= 85.2 grams of potassium chlorate.

CALCULATION OF PERCENTAGE COMPOSITION OF COMPOUNDS

If the formula of a compound and the atomic weights of the elements in the compound are known, it is easy to calculate the percentage of each element present.

Example—Calculate the percentage composition of potassium chlorate ($KClO_3$). [Atomic weights : K = 39, Cl = 35·5, O = 16.]

Molecular weight of $KClO_3 = 39 + 35.5 + 3 \times 16 = 122.5$

Percentage of potassium present $= \frac{39}{122.5} \times 100 = 31.83$

" chlorine " $= \frac{35.5}{122.5} \times 100 = 28.98$

" oxygen " $= \frac{48}{122.5} \times 100 = 39.18$

99.99

Example—Calculate the percentage composition of $Al_2(SO_4)_3$ (Aluminium Sulphate). [Atomic weights : Al = 27, S = 32, O = 16.]

Molecular weight of $Al_2(SO_4)_3 = 2 \times 27 + 3(32 + 4 \times 16)$
$= 54 + 288$
$= 342$

Percentage of aluminium present $= \frac{54}{342} \times 100 = 15.78$

" sulphur " $= \frac{3 \times 32}{342} \times 100 = 28.07$

" oxygen " $= \frac{3 \times 64}{342} \times 100 = 56.14$

99.99

CALCULATION OF FORMULA FROM PERCENTAGE COMPOSITION

If the percentages of the elements present are divided by the atomic weights of the elements, the numbers obtained are proportional to the number of atoms of each element present. The numbers obtained are usually not whole numbers. There cannot be fractions of atoms. Therefore we must find the smallest whole numbers which give the same proportion as the numbers found.

Example—A compound contains 42.11 per cent. of carbon, 6.43 per cent. of hydrogen, and 51.46 per cent. of oxygen. Find the simplest formula for the compound. [Atomic weights: C = 12, H = 1, O = 16.]

Divide by the atomic weights.

$$\text{Carbon} = \frac{42.11}{12} = 3.51 \text{ atoms of carbon}$$

$$\text{Hydrogen} = \frac{6.43}{1} = 6.43 \text{ ,, hydrogen}$$

$$\text{Oxygen} = \frac{51.46}{16} = 3.215 \text{ ,, oxygen}$$

To find the smallest whole numbers which give the same ratio make 3.215 = 1.

$$\text{Then Carbon} = \frac{3.51}{3.215} = 1.091$$

$$\text{Hydrogen} = \frac{6.43}{3.215} = 2.00$$

$$\text{Oxygen} = \frac{3.215}{3.215} = 1$$

By inspection we see that these numbers multiplied by 11 give whole numbers almost exactly.

Then Carbon = 12
Hydrogen = 22
Oxygen = 11

$\therefore$ Formula = $C_{12}H_{22}O_{11}$.

This formula is more complicated than most chemical formulæ, and therefore the calculation of formulæ is generally somewhat easier than in this example.

Example—Silver acetate was found on analysis to give the percentage composition C = 14.37, H = 1.79, O = 19.16, Ag = 64.68. [Atomic weight of Ag = 108.] Calculate the simplest formula for the compound.

Number of Atoms

$$\text{Carbon} \quad \frac{14.37}{12} = 1.2 \text{ very nearly}$$

$$\text{Hydrogen} \quad \frac{1.79}{1} = 1.8 \text{ ,,}$$

$$\text{Oxygen} \quad \frac{19.16}{16} = 1.2 \text{ ,,}$$

$$\text{Silver} \quad \frac{64.68}{108} = .6 \text{ ,,}$$

Divide through by .6, the smallest number of atoms.

$$\text{Then Carbon} = \frac{1.2}{.6} = 2$$

$$\text{Hydrogen} = \frac{1.8}{.6} = 3$$

$$\text{Oxygen} = \frac{1.2}{.6} = 2$$

$$\text{Silver} = \frac{.6}{.6} = 1$$

∴ Formula is $\mathbf{C_2H_3O_2Ag}$.

Example—Ferrous sulphate has the percentage composition $FeSO_4 = 54.68$, $H_2O = 45.31$. Find its formula. [Atomic weights: Fe = 56, S = 32, O = 16, H = 1.]

The molecular weight of $FeSO_4$ is $56 + 32 + 4 \times 16 = 152$.
The molecular weight of H_2O is $2 + 16 = 18$.

$$\therefore FeSO_4 = \frac{54.68}{152} = .359 \quad \text{Number of molecules of } FeSO_4$$

$$H_2O = \frac{45.31}{18} = 2.51 \quad \text{,,} \quad \text{,,} \quad H_2O$$

But 2.51 : .359 as 7 : 1 almost exactly.

∴ Formula is $\mathbf{FeSO_4.7H_2O}$.

CHAPTER IX

DETERMINATION OF MOLECULAR WEIGHTS AND ATOMIC WEIGHTS—VALENCY—NOMENCLATURE

DETERMINATION OF MOLECULAR WEIGHTS

Avogadro's Law indicates an easy method of determining the molecular weights of substances which are gaseous or can readily be turned into gases. If a glass tumbler is weighed, and then filled with marbles of equal size and weighed again, the weight of the marbles is obtained. If the marbles are replaced by spherical leaden bullets of the same size as the marbles, the weight of the bullets is obtained. The number of the bullets is the same as that of the marbles, because they occupy the same space. Therefore it is easy to calculate how many times a leaden bullet is heavier than a marble.

Similarly with gases. Since equal volumes of gases at the same temperature and pressure contain equal numbers of molecules, the number of times that a molecule of one gas is

heavier than a molecule of another can be determined by weighing equal volumes of the gases. This number is called the **density** of the gas. Therefore the densities of gases are proportional to the molecular weights of the gases. The density of hydrogen is taken as the standard and made equal to unity.

We know, therefore, in the case of a gas X, that

$$\frac{\text{Density of X}}{\text{Density of hydrogen}} = \frac{\text{Molecular weight of X}}{\text{Molecular weight of hydrogen}}$$

The density of hydrogen is 1 and the molecular weight of hydrogen is 2.

$$\therefore \frac{\text{Density of X}}{1} = \frac{\text{Molecular weight of X}}{2}.$$

$$\therefore \text{Molecular weight of X} = 2 \times \text{Density of X}.$$

The molecular weight of any gas is twice the density of the gas compared with hydrogen.

The method of finding the density of a gas by direct weighing has already been dealt with in the case of hydrogen. See Exp. 58.

DETERMINATION OF THE VAPOUR DENSITY OF A VOLATILE LIQUID BY VICTOR MEYER'S METHOD (FIG. 4)

Fig. 49 shows Victor Meyer's apparatus for determining the vapour density of volatile liquids or solids.

It consists of an outer glass tube **A**, in which is placed a liquid boiling at a temperature at least 30° C. above the boiling-point of the volatile liquid. The inner glass tube **B** has a long cylindrical bulb, at the bottom of which is placed some asbestos or dry sand to prevent the little bottle **C**, when introduced at **D**, from breaking the tube by its fall. A fine-bored side tube **E** leads to a graduated tube filled with water and inverted in a pneumatic trough.

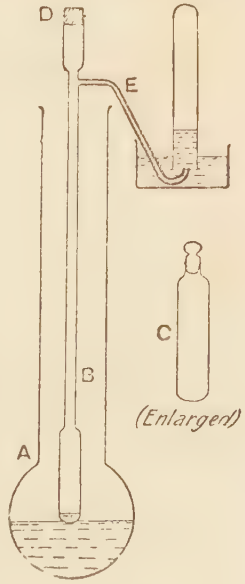


FIG. 49

The inner tube **B** is first thoroughly dried by heating gently

and by blowing air through it. The bottle **C** is weighed, filled with the necessary quantity of the volatile liquid and again weighed. The apparatus is put together, and the liquid in the outer tube is boiled until its vapour nearly fills the tube **A**. When air has ceased to bubble from the delivery tube **E**, the graduated tube is placed over the end of **E**, the cork **D** quickly removed, the bottle **C** dropped into the inner tube and the cork replaced. The liquid in **C** is converted to vapour, the stopper of **C** is blown out and the vapour drives out of **E** its own volume of air. The air is levelled and measured. The temperature of the water in which it is levelled is taken and the barometer is read.

Calculation—Let the weight of the volatile liquid be .25 gram.
Let the volume of air driven out be 47 c.c.
Temperature of water = 14° C. and pressure = 754 mm.
Water vapour pressure at 14° C. = 12 mm.

The volume of displaced air at 0° C. and 760 mm. is

$$47 \times \frac{273}{273+14} \times \frac{(754-12)}{760} = 43.6 \text{ c.c.}$$

∴ 43.6 c.c. of vapour at 0° C. and 760 mm. weigh .25 gram.

∴ 1 c.c. ,, ,, ,, weighs $\frac{.25}{43.6}$ gram.

But 1 c.c. of hydrogen at 0° C. and 760 mm. weighs .00009 gram.

$$\therefore \text{ Density of vapour} = \frac{.25}{43.6 \times .00009} = 63.6$$

Therefore the molecular weight of the compound is 2×63.6.

$= 127.2.$

Useful liquids for the outer tube in Victor Meyer's method are: water, boiling-point 100° C.; acetic acid, boiling-point 119° C.; aniline, boiling-point 180° C.

DETERMINATION OF MOLECULAR WEIGHT BY LOWERING OF FREEZING-POINT

The molecular weights of non-volatile substances can frequently be determined by observing the lowering of the freezing-point or raising of the boiling-point, caused by dissolving in a solvent a weighed amount of the substance. It has been found that molecular weights of substances* which do not split up in solution, when dissolved in a fixed amount of the same solvent always give exactly the same lowering of

* This method cannot be used for the determination of the molecular weights of metallic salts. Salts are partly split up, or ionised, when dissolved in water.

freezing-point. There must of course be no chemical action between the dissolved substance and the solvent.

The lowering produced in 100 grams of the solvent by the solution of a gram molecular weight of the substance is the constant K for that particular solvent.

For water the constant K is 19, for acetic acid 39, for benzene 49, etc. This means that if a molecular weight of sugar, 342 grams, were dissolved in 100 grams of water, the water would then freeze at $-19°$ C.

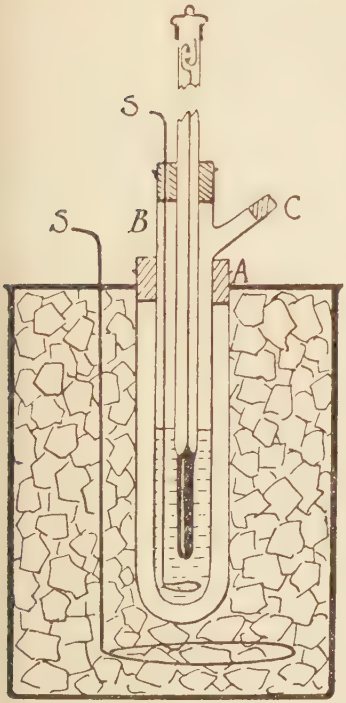


FIG. 50

The apparatus used is shown in Fig. 50.

It consists of an outer tube **A**, immersed in a bath of some freezing mixture containing a stirrer **S**. Into **A** is fitted an inner tube **B**, which is provided with a side tube **C**, and is fitted with a stirrer **S** and a delicate thermometer reading to $\frac{1}{100}$ of a degree centigrade. There is therefore an air space between the two tubes.

About 25 to 30 grams of solvent are weighed into the inner tube **B** and the tube placed in the outer tube. The liquid is cooled down well below its freezing-point and then vigorously stirred. It begins to solidify, and the mercury in the thermometer rapidly rises to the freezing-point, at which it remains steady. Next, a weighed amount of the substance, about .2 to .3 gram, is introduced through **C**, and the inner tube gently warmed until all the substance is dissolved. The freezing-point of the solution is next determined.

Let W be weight of solvent, w be weight of substance, M be molecular weight of substance, l be lowering of freezing-point, K the constant for the liquid. The value of K is known.

Then a lowering of l° is produced by solution of w grams of substance in W grams of solution.

$\therefore$ A lowering of $\frac{l^\circ}{w}$ is produced by solution of 1 gram of substance in W grams of solution.

$\therefore$ A lowering of $\frac{l}{w} \times W^\circ$ is produced by solution of 1 gram of substance in 1 gram of solution since the solution becomes W times as strong.

$\therefore$ A lowering of $\frac{l \times W^\circ}{w \times 100}$ is produced by solution of 1 gram of substance in 100 grams of solution.

$\therefore$ A lowering of $\frac{l \times W}{w \times 100} \times M^\circ$ is produced by solution of M grams of substance in 100 grams of solution.

But this lowering is the molecular lowering, *i.e.* is equal to the constant K, of which the value is known.

$$\therefore \frac{l \times W \times M}{w \times 100} = K \quad \therefore M = \frac{100 \times w \times K}{l \times W}.$$

VALENCY

The atoms of the elements have different capacities for combining with atoms of other elements. One atom of hydrogen cannot combine with more than one atom of any element. An atom of oxygen can combine with two atoms of hydrogen, or two atoms of chlorine, or one atom of magnesium. One atom of phosphorous can combine with five atoms of chlorine, and one atom of osmium with four atoms of oxygen.

An element, one atom of which is capable of combining directly with only one atom of any other element, is known as a *monad* or *monovalent element*. If one atom of an element can combine with two atoms of a monad element, it is called a *diad* or *divalent element*; if with three atoms of a monad element, it is called a *triad* or *trivalent element*, and so on.

The number of monad atoms with which one atom of an element can combine directly is known as the valency *of that element.*

Thus the following formulæ show the valency of four elements towards hydrogen.

HCl	Hydrochloric acid	Chlorine is monovalent
H_2O	Water	Oxygen is divalent
H_3N	Ammonia	Nitrogen is trivalent
H_4C	Marsh gas	Carbon is tetravalent

No element has towards hydrogen a greater valency than 4. Towards oxygen an element may have a valency up to 8.

Thus—

Na_2O	Sodium oxide	Sodium is monovalent
ZnO	Zinc oxide	Zinc is divalent
Al_2O_3	Aluminium oxide	Aluminium is trivalent
SiO_2	Silicon oxide	Silicon is tetravalent
Sb_2O_5	Antimony oxide	Antimony is pentavalent
SO_3	Sulphur trioxide	Sulphur is hexavalent
Cl_2O_7	Chlorine heptoxide	Chlorine is heptavalent
OsO_4	Osmium tetroxide	Osmium is octavalent

The maximum valency of an element is often not exerted. For instance, sulphur has a maximum valency of 6. In sulphur dioxide, SO_2, it has only a valency of 4. Carbon, with a maximum valency of 4, has in carbon monoxide, CO, a valency of 2, unless oxygen is tetravalent in this compound.

The valency of an element may also be defined as the atomic weight of the element divided by the equivalent weight.

Thus—Atomic weight of oxygen = 16. Equivalent = 8.

$$\text{Valency} = \frac{16}{8} = 2.$$

Atomic weight of aluminium = 27. Equivalent = 9.

$$\text{Valency} = \frac{27}{9} = 3.$$

An atom of nitrogen will combine with three atoms of hydrogen. We define equivalent as the amount of an element which will combine with 1 part by weight of hydrogen. Therefore a third of the atomic weight of nitrogen will combine with 1 part by weight of hydrogen. Therefore the atomic weight of nitrogen is 3 times its equivalent weight, and nitrogen is trivalent.

Again, an atom of carbon combines with 2 atoms of oxygen. Equivalent weight may be defined as the weight of the element which combines with 8 parts of oxygen. One atom of oxygen weighs 16. Therefore $\frac{1}{2}$ of the atomic weight of carbon combines with 8 parts of oxygen. That is to say, the atomic weight of carbon is four times its equivalent weight, and carbon is tetravalent. The following list shows the valency of the commoner elements and groups of elements. The valency given is that occurring in most of the compounds of

the elements. It will be noticed that several elements are placed in more than one class. In these cases the elements form two or more series of common compounds.

Monads	Diads	Triads	Tetrads	Pentads	Hexads	Heptads	Octads
Hydrogen	Oxygen	Nitrogen	Carbon	Nitrogen	Sulphur	Chlorine	
Chlorine	Zinc	Phosphorus	Silicon	Phosphorus	Chromium	Iodine	
Iodine	Calcium	Aluminium	Lead	Arsenic		Bromine	
Potassium	Tin	Ferric iron	Tin	Antimony			
Silver	Magnesium	Gold	Platinum				
Gold	Copper	Chromium	Chlorine				
Bromine	Platinum	Arsenic	Sulphur				
Sodium	Sulphur	Antimony					
Ammonium	Barium	Phosphate					
Copper	Lead						
Nitrate	Ferrous iron						
Acetate	Sulphate						
Hydroxyl	Oxalate						

DETERMINATION OF ATOMIC WEIGHTS.

The accurate determination of atomic weights of the elements is very important to chemists. Equivalent weights can be found very accurately. We have seen that $\frac{\text{atomic weight}}{\text{equivalent weight}}$ = valency, a small whole number. If, then, the equivalent weight of an element is determined accurately and the valency approximately, the atomic weight can be found accurately by multiplying the equivalent weight by the valency. This is made use of in Dulong and Petit's method of determining atomic weights.

(1) **Method of Dulong and Petit**

In 1819, Dulong and Petit stated their law—*the atoms of all substances have exactly the same capacity for heat.* The law may be stated—*the atomic weight of an element, multiplied by its specific heat in the solid state, is a constant.*

The constant, known as the *atomic heat,* has been found to be approximately 6.4, and the law has been found to be approximately true for most elements. Thus, the specific heat of mercury is .0319 and its atomic weight 200.

$$.0319 \times 200 = 6.38.$$

Specific heat of copper = 0952. Atomic weight of copper = 63.

$$.0952 \times 63 = 5.99.$$

Let us apply the law to the determination of the accurate

atomic weight of an element which has a specific heat of .087 and an equivalent of 38.5.

$$\text{Approximate atomic weight} = \frac{6.4}{.087} = 73.$$

$$\text{Now, } \frac{\text{atomic weight}}{\text{equivalent weight}} = \text{valency}; \quad \therefore \quad \text{valency} = \frac{73}{38.5} = 1.89.$$

Valency must, of necessity, be expressed by a whole number, because atoms cannot combine with fractions of atoms, and valency is defined as the number of monavalent atoms with which one atom of an element will combine.

1.89 is nearly 2. Errors of experiment and of Dulong and Petit's Law are quite sufficient to account for the difference between 1.89 and 2. Therefore the valency is most probably 2.

And the accurate atomic weight = valency × equivalent weight
$= 2 \times 38.5$
$= 77.$

Example (1)—.3697 gram of a metal, on solution in hydrochloric acid, liberated .04106 gram of hydrogen. The specific heat of the metal is .225. Calculate the accurate atomic weight of the metal.

$$\text{Equivalent weight of the metal} = \frac{.3697}{.04106} = 9.004.$$

$$\text{Approximate atomic weight of metal} = \frac{6.4}{.225} = 28.4 \text{ (nearly)}.$$

$$\therefore \text{ Valency of metal} = \frac{\text{atomic weight}}{\text{equivalent weight}} = \frac{28.4}{9.004} = 3 \text{ (nearly)}.$$

$$\therefore \text{ Accurate atomic weight} = 3 \times 9.004 = 27.012.$$

Example (2)—Erdmann and Marchand obtained 109.6308 grams of mercury from 118.3938 grams of the red oxide. The specific heat of mercury is .0319. Calculate the accurate atomic weight of mercury.

Let x be the equivalent weight of mercury. x grams of mercury must be combined with 8 grams of oxygen in the red oxide. Then $x+8$ grams of red oxide give x grams of mercury.

$$\therefore \frac{x+8}{x} = \frac{118.3938}{109.6308} \quad \therefore x = 100.1$$

$$\text{Rough atomic weight of mercury} = \frac{6.4}{\text{specific heat}} = \frac{6.4}{.0319} = 200.6 \text{(nearly)}.$$

$$\therefore \text{Valency} = \frac{\text{atomic weight}}{\text{equivalent weight}} = \frac{200.6}{100.1} = 2 \text{ (nearly).}$$

$$\therefore \text{Accurate atomic weight} = 2 \times 100.1 = 200.2.$$

(2) **Method based on Avogadro's Law**

Another method used for the determination of atomic weights is founded on Avogadro's Law. In a number of compounds of the element it is very probable that at least one compound will contain only one atom of the element in a molecule. A number of compounds of an element are analysed, and the molecular weights of those compounds determined. The smallest weight of the element found in a molecular weight of any of its compounds therefore is probably the atomic weight of the element. Of course, in the future some compound of the element may be discovered which contains a smaller weight of the element than is contained in a molecular weight of any of its known compounds. If such a compound be discovered, the new weight of the element contained in the molecular weight of the compound will be taken as the atomic weight.

We may therefore state that *the smallest weight of an element contained in the molecular weight of any of its compounds is the maximum atomic weight of that element.* The atomic weight may be less, but cannot be greater, than this number.

The molecular weight of volatile compounds is easily determined by finding the vapour densities and multiplying by 2 (see page 105). An example will illustrate the method

Names of Compounds	*Density*	*Molecular weight*	*Weight of element in a molecular weight*
Carbon dioxide	22	44	12
Carbon monoxide	14	28	12
Carbon bisulphide	38	76	12
Ethylene	14	28	24
Alcohol	23	46	24
Acetone	29	58	36
Ether	37	74	48

The smallest weight of carbon in a molecular weight of the compounds given is 12. In no known compound of carbon

is there found less than 12 parts of carbon in a molecular weight of the compound.

Therefore 12 is the maximum value for the atomic weight of carbon. If a compound containing 6 parts of carbon in the molecular weight is discovered, the maximum atomic weight of carbon will then be taken as 6. Such a discovery is very unlikely, however, because Dulong and Petit's Law also indicates that the atomic weight of carbon is 12.

For a description of the other methods used by chemists for the determination of atomic weights, more advanced books must be consulted.

CHEMICAL NOMENCLATURE

Unfortunately the naming of chemical elements and compounds is not entirely systematic, owing to the discovery and naming of many substances before a systematic method was developed.

The names of metals usually end in *-um*. This is not the case with Lead, Copper, Iron, Gold, Silver, Tin. The Latin names of these metals, from which they take their symbols, do, however, end in *-um*: Plumbum, Cuprum, Ferrum, Aurum, Argentum, Stannum.

The rest of the elements are non-metals. The modern practice is to make names of non-metals end in *-on*. Thus Argon, Carbon, Boron, Silicon, etc., are names of non-metals.

When a compound is built up of two elements, the name of one of the elements is made to end in *-ide*. It is the name of the non-metallic part which is thus modified.

Thus—	CaO	Calcium oxide
	HgS	Mercuric sulphide
	SbH_3	Antimony hydride
	CaC_2	Calcium carbide
	$NaCl$	Sodium chloride

Prefixes are used to distinguish between two or more compounds of the same elements.

Thus—	Nitrogen monoxide	N_2O
	Nitrogen trioxide	N_2O_3
	Nitrogen pentoxide	N_2O_5
	Lead monoxide	PbO
	Lead dioxide	PbO_2

Sometimes the name of the metal is modified by the termination *-ous* and *-ic*. The name of the salt in which the metal has the higher valency has the termination *-ic*.

Ferrous sulphate	$FeSO_4$	Stannous chloride	$SnCl_2$
Ferric sulphate	$Fe_2(SO_4)_3$	Stannic chloride	$SnCl_4$

The names of salts of acids ending in *-ic* are ended with *-ate*, of acids ending in *-ous* with *-ite*.

Thus—Sulphuric acid forms sulphates
Sulphurous acid forms sulphites
Phosphoric acid forms phosphates
Phosphorous acid forms phosphites

One exception is hydrochloric acid, which gives salts known as chlor*ides*, but these salts are composed of only two elements.

Substances which may be regarded as derived from water, by replacement of one of the hydrogen atoms in each molecule of water by a metal, are called *hydroxides*.

HOH	NaOH	$Fe(OH)_2$	$Al(OH)_3$
Water	Sodium hydroxide	Ferrous hydroxide	Aluminium hydroxide

The name "hydrate" was formerly used in place of "hydroxide." Thus, the terms sodium hydrate and calcium hydrate were employed in place of the terms sodium hydroxide and calcium hydroxide. *Hydrate* should only be used for substances, like salts, which contain water of crystallisation. Thus $FeSO_4\ 7H_2O$ is the hydrated form of ferrous sulphate. In other words, ferrous sulphate forms a hydrate with water, containing seven molecules of water of crystallisation.

PART II

General directions for determining the properties of a gas

(1) Notice colour, smell, taste.

(2) Test the solubility by inverting a jar in water and allowing it to stand.

(3) Shake up with litmus to determine whether the gas is acid or alkaline.

(4) Try to burn the gas.

(5) Introduce a burning taper, sulphur, phosphorus, magnesium, sodium, into the gas to see whether it supports combustion.

(6) Try to determine whether the gas is heavier or lighter than the air by pouring it upwards or downwards from one jar to another, and afterwards testing both jars for the gas.

(7) Determine special properties of the gas according to the directions given for each gas.

CHAPTER X

HYDROGEN—GRAHAM'S LAW OF DIFFUSION

Exp. 71—To prepare hydrogen and examine its properties

Prepare hydrogen from zinc and dilute sulphuric acid (1 part of acid to 4 of water).

Determine the ordinary properties of the gas.

Find the proportions of hydrogen and air which give the best explosive mixture, by filling a strong tube with various proportions of the gases and exploding the mixture.

Pass hydrogen over copper oxide heated to redness in a hard glass tube. Collect and examine the products.

Filter the residue from the preparation of hydrogen, and by evaporating try to obtain crystals of the salt which is in solution.

HYDROGEN. Symbol, H.

Occurrence—Hydrogen occurs in nature in enormous quantities. The air contains 1 part of free hydrogen in about 10,000 parts of air. Water contains $\frac{1}{9}$ of its weight of hydrogen. All animals and plants contain hydrogen in varying proportions.

Formation—(1) From water by electrolysis. Water will not conduct a current of electricity. And so a few drops of sulphuric acid are added to make the water conduct, and a current from 4 or 5 cells is passed between platinum electrodes. The hydrogen is evolved at the kathode or negative electrode, and oxygen at the anode or positive electrode.

$$2H_2O = 2H_2 + O_2$$

The amount of sulphuric acid present is the same at the beginning and end of the experiment.

(2) From water or steam by the action of metals.

The alkali metals, sodium and potassium, readily decompose water at ordinary temperatures, giving hydrogen and the hydroxides of the metals. The hydroxides of the metals remain in solution. Sodium floats, melts, and moves about on the surface of the water, giving off hydrogen. When potassium is used, the heat of the reaction is sufficiently great to light the hydrogen given off. The potassium colours the flame lilac. In both cases the hydrogen may be collected if the metal is held under the mouth of an inverted cylinder by means of a wire gauze spoon, Fig. 51.

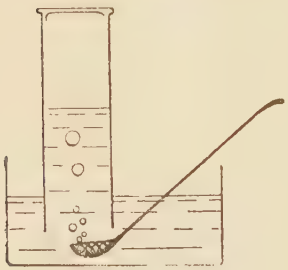


FIG. 51

$$2H_2O + 2Na = H_2 + 2NaOH$$
Sodium — Sodium hydroxide

$$2H_2O + 2K = H_2 + 2KOH$$
Potassium — Potassium hydroxide

If steam is passed over red-hot iron, zinc, or magnesium, hydrogen is readily obtained. The apparatus used is shown in Fig. 52.

$$\underset{\text{Zinc}}{Zn} + \underset{\text{Water}}{H_2O} = \underset{\text{Zinc oxide}}{ZnO} + H_2$$

$$\underset{\text{Magnesium}}{Mg} + \underset{\text{Water}}{H_2O} = \underset{\text{Magnesium oxide}}{MgO} + H_2$$

$$\underset{\text{Iron}}{3Fe} + \underset{\text{Water}}{4H_2O} = \underset{\text{Magnetic oxide of iron}}{Fe_3O_4} + 4H_2$$

(3) Hydrogen is most conveniently prepared by the action

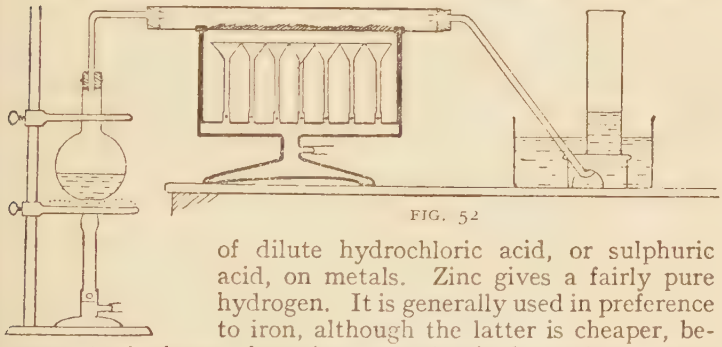


FIG. 52

of dilute hydrochloric acid, or sulphuric acid, on metals. Zinc gives a fairly pure hydrogen. It is generally used in preference to iron, although the latter is cheaper, because the hydrogen from iron contains hydro-carbons (compounds of hydrogen and carbon) derived by the interaction of the carbon present in the iron with the nascent hydrogen. The hydrogen from zinc may be purified by passing it through a wash-bottle containing a solution of potassium permanganate.

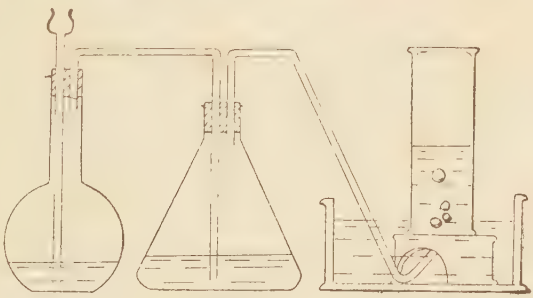


FIG. 53

$$\underset{\text{Hydrochloric acid}}{Zn + 2HCl} = \underset{\text{Zinc chloride}}{ZnCl_2} + H_2$$

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

Sulphuric acid — Zinc sulphate

By evaporation of the residue from the preparation of hydrogen from zinc and sulphuric acid, crystals of zinc sulphate can readily be obtained.

Properties—Density = 1. Atomic weight = 1. Molecular weight = 2. Solubility = almost insoluble. Boiling-point = − 252 to − 253° C. Melting-point = − 256 to − 257°C. 1 litre at 0° C. and 760 mm. weighs .09 gram.

Hydrogen is a colourless gas without smell or taste. It is not poisonous, but animals cannot live in it, because they require oxygen. It is the lightest substance known. Its extreme lightness may be shown by filling soap bubbles with the gas; or if you fill with it an inverted beaker suspended from the arm of a balance, the arm carrying the beaker slowly rises as the air in the beaker is displaced by hydrogen.

Hydrogen burns with a very hot, pale-blue flame, combining with the oxygen of the air to form water.

$$2H_2 + O_2 = 2H_2O.$$

The water from a burning jet of hydrogen may be collected in the bulb of the apparatus shown in Fig. 54.

Hydrogen will not, however, allow ordinary combustibles to burn in it. A jet of oxygen may readily be burnt in the gas by inverting a jar of hydrogen, lighting the gas at the mouth of the jar, and then slowly introducing the jet. The very high temperature of the flame of hydrogen burning in oxygen is made use of in the oxy-hydrogen blow-pipe, in which a stream of oxygen is blown through the flame of burning hydrogen.

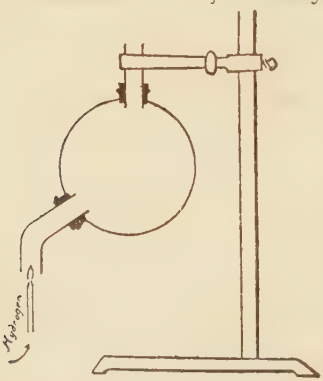


FIG. 54

Two volumes of hydrogen, mixed with one volume of oxygen, make a violently explosive mixture. Similarly, two volumes of hydrogen form an explosive mixture with five volumes of air.

Hydrogen is a powerful reducing agent, that is, *it is capable of combining with and reducing the proportion of the non-*

metallic portion of a number of compounds. Thus hydrogen passed over some metallic oxides, heated to redness, reduces the oxides to metal.

$$\text{Cupric oxide, } CuO + H_2 = Cu + H_2O$$

$$\text{Magnetic oxide of iron, } Fe_3O_4 + 4H_2 = 3Fe + 4H_2O$$

The second equation is the reverse of that representing the preparation of hydrogen from iron and steam. The action is reversible. In the above reaction the excess of hydrogen carries away the steam as fast as it is produced. When hydrogen is prepared by passing steam over heated iron, the excess of steam carries away the hydrogen as fast as it is produced. In fact, difference in the conditions causes the reaction to take place in opposite ways.

Hydrogen is used for conversion of oils, in the presence of finely divided nickel, into margarine ; for filling airships and balloons ; in *coal gas*, which contains about half its volume of hydrogen, for lighting and heating purposes ; in *water gas*, which consists chiefly of hydrogen and carbon monoxide, as a fuel ; and for the preparation of ammonia by the Haber process.

Nascent hydrogen

Hydrogen is particularly active as a reducing agent when it is nascent, or is being born. For example, ordinary hydrogen passed into a solution of ferric chloride, $FeCl_3$, has no action. If, however, the hydrogen is made within the solution from zinc and dilute sulphuric acid, the ferric chloride is reduced to ferrous chloride, $FeCl_2$.

$$FeCl_3 + H = FeCl_2 + HCl.$$

The proportion of chlorine, the non-metallic part of the compound, is reduced. It will be noticed that in the equation hydrogen is written H, not H_2. This is intended to indicate that the atoms of hydrogen, at the time of reaction with ferric chloride, have not yet combined together to form ordinary molecular hydrogen, H_2. It is easy to understand that hydrogen will be more active before the atoms have combined together to form molecules, for, before molecular hydrogen can combine with other substances, the molecules must be split up. Other substances are also found to be more active when nascent.

DIFFUSION OF HYDROGEN. GRAHAM'S LAW

If a jar of hydrogen be uncovered and left for a few minutes in the room free from draught, the gas completely leaves the jar, whether the jar be upright or inverted : the hydrogen has escaped into the air by the process called **diffusion.**

Graham found that the rates of diffusion of gases were different and depended on the densities of the gases. He filled bottles, fitted with stoppers carrying narrow glass tubes,

with gases of varying densities. The tubes were pointed downwards in the case of light gases, and upwards for heavy gases, and the contents were allowed to diffuse into the air for a given time. He afterwards analysed the contents of the bottles. He found that hydrogen diffused more rapidly than any other gas. Carbon dioxide diffused at only about one-fifth of the rate of hydrogen. He established the law that—*the rates of diffusion of gases are inversely proportional to the square roots of their densities.*

The density of hydrogen is 1, of oxygen 16, of carbon dioxide 22, and of chlorine 35.5.

∴ The rates of diffusion of these gases are in the ratio

$$\frac{1}{\sqrt{1}} : \frac{1}{\sqrt{16}} : \frac{1}{\sqrt{22}} : \frac{1}{\sqrt{35.5}}$$

$$= 1 : \frac{1}{4} \quad \frac{1}{4.7} : \frac{1}{6} \text{ approximately.}$$

This means that hydrogen diffuses 4 times as rapidly as oxygen, 4.7 times as rapidly as carbon dioxide, and 6 times as rapidly as chlorine.

The great rate of diffusion of hydrogen compared with that of air may be demonstrated by the apparatus shown in Fig. 55.

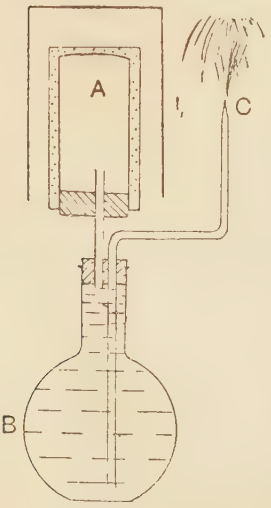


FIG. 55

A is a porous earthenware pot fitted with an india-rubber cork, and a tube leading to **B**, a vessel filled with water. From **B** passes a jet **C**.

A jar full of hydrogen is placed round **A**. The hydrogen passes through the pores of **A** much more quickly than the air leaves **A**. Therefore gas passes down into **B** and forces out water through the jet **C**. When the hydrogen jar is removed, the hydrogen in **A** escapes more quickly than the air gets in, and consequently air is drawn into **B** through the jet **C**.

Fig. 56 shows an apparatus which is useful for comparing the rates of diffusion of gases.

A narrow tube **A**, about 33 inches long, is sealed to a wider tube **B**, which is provided with a tight-fitting india-rubber cork and two delivery tubes.

The tube **A** is filled at the top with a porous plug of plaster of Paris. The lower end dips into mercury. The air is first exhausted from **A** and **B** by means of a good mercury pump with the clip **C** closed. The height of the mercury column in **A** is then read with the strong clips **C** and **D** closed. **C** is then opened to a reservoir of the gas, and the time taken by the mercury column to fall to a fixed point in **A** is noted. **A** and **B** are then again exhausted and put into connexion with a second gas. The time taken by the column to fall through the same distance is again noted.

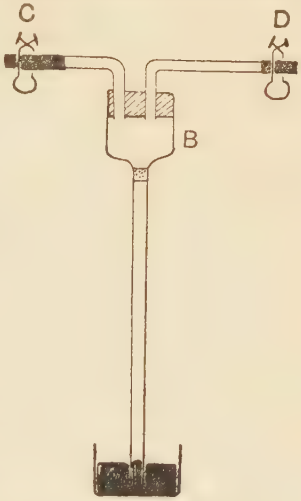


FIG. 56

The more quickly a gas diffuses, the shorter is the time taken by the mercury to fall. Therefore the times will be inversely proportional to the rates of diffusion of the gases.

Let times and rates be t_1, t_2 ; r_1, r_2. Then $\frac{t_1}{t_2} = \frac{r_2}{r_1}$.

CHAPTER XI

WATER AND HYDROGEN PEROXIDE

Exp. 72—To make a supersaturated solution of a salt

Directions—Dissolve crystals of sodium sulphate or sodium thiosulphate in about 10 c.c. of water kept hot, until no more salt will dissolve. Filter into a perfectly clean flask ; stop up the neck of the flask with cotton wool. Let the flask and its contents stand in cold water until quite cold.

Next, carefully remove the cotton wool and drop into the

flask a small crystal of the salt used. Note the rise in temperature as the salt crystallises. Explain the rise.

Exp. 73—To show the decrease of solubility of calcium citrate with rise of temperature

Directions—Make a solution of 12 grams of citric acid in 15 c.c. of water, and add strong ammonia solution until the solution is neutral to litmus paper. Next dissolve 20 grams of crystallised calcium chloride, or 10 grams of anhydrous calcium chloride in 20 c.c. of water. Mix the two solutions in the cold and shake. Now gently warm the mixture. A precipitate of calcium citrate forms. If the solution be quickly cooled again this precipitate will disappear. On heating more strongly the mixture goes practically solid from the precipitation of calcium citrate.

Exp. 74—To show the effect of water of crystallisation on the colour of some salts

Directions—

(1) Warm gently a few copper sulphate crystals until white. Allow to cool, and add a few drops of water.

(2) Gently warm, in a dry test-tube, a few crystals of cobalt chloride. Allow to cool, and shake up with a few drops of water.

(3) Make a dilute solution of cobalt chloride, moisten with it some white paper, and allow the paper to dry. Next warm the paper.

(4) Add a solution of potassium iodide to a solution of cobalt chloride and carefully evaporate to dryness in a small porcelain dish.

(5) Make a solution of cobalt chloride in alcohol. Add water to the solution. Explain the changes of colour.

Exp. 75—To find the number of molecules of water of crystallisation in a molecule of crystallised magnesium sulphate

Directions—Weigh a dry crucible and lid. Into the crucible put one or two grams of magnesium sulphate and weigh again. Heat the crucible and its contents, at first gently and then to low redness. Weigh again. Heat once more and weigh again. Repeat the heating and weighing until the weight is constant.

Calculate as follows :—

Let x = number of molecules of water of crystallisation in one molecule of magnesium sulphate.

Then the formula of the crystallised sulphate must be $MgSO_4.xH_2O$.

Then

$$\frac{\text{weight of } MgSO_4.xH_2O}{\text{weight of } MgSO_4} = \frac{\text{weight of crystallised salt taken}}{\text{weight of anhydrous salt left}}$$

$$\therefore \frac{24+32+4\times16+x(2+16)}{24+32+4\times16} = \frac{\text{weight of crystallised salt taken}}{\text{weight of anhydrous salt left}}$$

In this equation everything is known except x. Find x.

Exp. 76—To make a dilute solution of hydrogen peroxide and find out its properties

Directions—To 30 or 40 c.c. of cold dilute hydrochloric acid in a beaker add 3 or 4 grams of barium peroxide, a small quantity at a time. Stir for some time. Filter if necessary.

Carry out the following tests with portions of the solution :—

(1) Gently warm a portion and test the evolved gas for oxygen.

(2) Add a few drops of potassium permanganate solution. Note change of colour and test gas evolved for oxygen.

(3) Dip a piece of filter paper into lead acetate solution, allow a bubble of sulphuretted hydrogen to form lead sulphide with the lead acetate, and then leave the blackened paper in hydrogen peroxide solution.

(4) Acidify a solution of potassium bichromate with a few drops of dilute sulphuric acid, add 2 or 3 c.c. of ether and a few drops of hydrogen peroxide solution. Shake up and note the colour of the ether.

(5) Try whether hydrogen peroxide solution will bleach indigo. Use only one or two drops of indigo solution with 4 or 5 c.c. of hydrogen peroxide solution and warm the mixture.

WATER

Properties—Formula = H_2O. Molecular weight = 18. Vapour density = 9. Specific gravity = 1. Freezing-point = 0° C. Boiling-point = 100° C.

Water is, when pure, a liquid without taste or smell. In small quantities it is colourless. In large quantities it is

greenish-blue. The intense blue colour of the Swiss lakes is probably largely due to the scattering of blue light by the exceedingly fine particles of mud brought down by the rivers from the glaciers. These particles are so small that they remain suspended in the water for a very long time.

Water is a very bad conductor of heat. Water at the top of a test-tube may be boiled without causing any appreciable rise of temperature in the water at the bottom of the tube.

Water is almost incompressible. An increase of 1 atmosphere pressure on 100,000 volumes of water only reduces the volume to 99,995 volumes. Although this decrease of volume is so small, yet it has been calculated that if water were to become quite incompressible, the level of the sea would rise over 100 feet, and 2,000,000 square miles of land would be submerged.

Water is most dense at 4° C. When it is cooled below 4° C. its volume increases until it becomes ice, when its volume suddenly increases by $\frac{1}{10}$. This fact has an important influence in nature. If ice did not float on water, each layer of ice as it formed would sink to the bottom of our rivers and lakes, so that in a long spell of frost, rivers and lakes would become a solid mass of ice, the fish in them would be exterminated and even the heat of summer would not melt the ice. As things actually are, the layer of ice on the surface makes the cooling of the water very slow. The temperature of the water at the bottom of deep rivers and lakes never falls below 4° C., and fish can live in water at that temperature.

Solubility of solids and liquids

Water will dissolve a greater number of solids than any other solvent. Probably no solid is perfectly insoluble in water, but no solid will dissolve in water to an unlimited extent. Silver chloride is one of the most insoluble of salts, yet it dissolves to the extent of one part of silver chloride in about a million parts of water. Many of the metals are so insoluble that the most delicate tests are unable to detect their presence in water to which they have been exposed. Cane sugar is one of the most soluble of solids. It dissolves in one-third of its weight of water at ordinary temperatures.

Almost all substances are more soluble in hot than in cold water. Thus 100 parts of water dissolve 13 parts of potassium

nitrate at 0° C., and 245 parts at 100° C.; 35 parts of sodium chloride at 0° C., and 40 parts at 100° C. Other salts, with few exceptions, behave in a similar way. The few exceptions, which are more soluble in cold than in hot water, include calcium hydroxide, calcium citrate, and sodium sulphate.

Some solutions of salts, when saturated at a high temperature and cooled down, without shaking, to ordinary temperatures, do not crystallise. When, however, a small crystal of the salt is added to such a solution, the excess of dissolved salt over that required to saturate the water at ordinary temperature at once crystallises out with evolution of heat. Sodium sulphate, sodium thiosulphate, and sodium acetate readily form such *supersaturated solutions*. The solution should be cooled down in a perfectly clean flask, and protected from dust particles by cotton wool placed in the neck of the flask.

Some liquids are soluble in all proportions in other liquids. Thus, water and alcohol, alcohol and ether, mix together in any proportion. Ether, however, will only dissolve about 3 per cent. of water, and water will dissolve only about 10 per cent. of ether at ordinary temperatures. The solubility of liquids in liquids increases as the temperature rises.

Solubility of gases

The solubility of gases in water decreases as the temperature rises. Most gases are completely expelled from solution by boiling, but hydrochloric acid, hydrobromic acid, and hydriodic acid are exceptions. When a weak solution of hydrochloric acid is boiled under ordinary pressure, water is given off until the solution contains about 20 per cent. of the acid, when the solution distils unchanged. Moreover, a strong solution gives off hydrochloric acid when boiled, until an acid of the same strength (about 20 per cent.) is obtained. The solubilities of some of the common gases are given in the following table :—

	Volume of gas dissolved by 1 c.c. of water at 0° C. and 760 mm.		Volume of gas dissolved by 1 c.c. of water at 0° C. and 760 mm.
Hydrogen	0.019	Sulphuretted hydrogen	4.370
Nitrogen	0.020	Sulphur dioxide	79.8
Oxygen	0.041	Hydrochloric acid	503.0
Carbon dioxide	1.800	Ammonia	1149.0

It was found by **Henry** that *the weight of gas dissolved by water is directly proportional to the pressure, except in the case of the very soluble gases.* Thus oxygen under a pressure of 10 atmospheres would be ten times as soluble as oxygen under the ordinary pressure. Soda water is charged with carbon dioxide under a pressure of several atmospheres. Consequently, when the pressure is made equal to atmospheric pressure by opening the bottle, most of the carbon dioxide escapes with effervescence.

Dalton discovered what is known as the **Law of Partial Pressures.** This law states that *the solubility of a gas contained in a mixture of gases is proportional to its partial pressure.* The partial pressure of a gas is that part of the pressure of the mixture which is caused by the gas. Thus, oxygen, in a mixture of 20 volumes of oxygen and 80 volumes of nitrogen, would cause a pressure only one-fourth of that caused by the nitrogen. Oxygen is twice as soluble as nitrogen. Therefore, if such a mixture were dissolved in water, in a litre of water there would be $\frac{20}{100} \times 1000 \times .041 = 8.2$ c.c. of oxygen, and $\frac{80}{100} \times 1000 \times .020 = 16$ c.c. of nitrogen. Therefore the percentage of oxygen in the gas boiled out from solution in water would be about 32.8.

Water of crystallisation

We have seen that a number of salts when crystallised from solution in water contain water of crystallisation. The number of molecules of water taken up by a molecule of salt is always the same if the salt is crystallised under the same conditions, but the number may vary under different conditions.

Thus, sodium carbonate crystallises at ordinary temperatures with 10 molecules of water, forming crystals of the composition $Na_2CO_3.10H_2O$. If the salt is crystallised between 30° and 50° C., the crystals have the composition $Na_2CO_3.7H_2O$.

Some salts, like $Na_2CO_3.10H_2O$ and $Na_2SO_4.10H_2O$, give off the whole or part of their water of crystallisation if exposed to the air at ordinary temperatures. Such salts are said to *effloresce* and the salts are said to be *efflorescent.*

Other salts, like calcium chloride, take up sufficient moisture

from the air to dissolve the salt. Such salts are said to *deliquesce* and the salts are said to be *deliquescent.*

Other substances will take up some moisture from the air, but not enough to dissolve them. They are said to be *hygroscopic.*

Your experiments with copper sulphate, cobalt chloride, and cobalt iodide (formed by adding potassium iodide solution to cobalt chloride solution) have shown you that water has sometimes much to do with the colour of a salt.

Anhydrous copper sulphate, $CuSO_4$, is white ; $CuSO_4.5H_2O$ is blue. Anhydrous cobalt chloride, $CoCl_2$, is blue ; $CoCl_2.6H_2O$ is pink. Anhydrous cobalt iodide, CoI_2, is almost black ; $CoI_2.2H_2O$ and $CoI_2.4H_2O$ are green, and $CoI_2.6H_2O$ is dark red. Solutions of cobalt chloride have been used for "sympathetic inks." The faint pink obtained by writing on paper with a weak solution is almost invisible. When the paper is warmed a distinct blue makes its appearance, and the blue disappears when the salt is allowed to take up moisture again from the air.

Composition of water by weight

In Exp. 64 the composition of water by weight was determind. Dry, fairly pure hydrogen was passed over heated

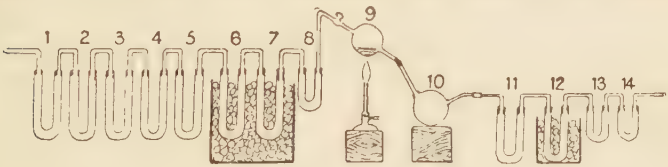


FIG. 57

copper oxide, and the weight of water collected in the calcium chloride tube was determined. The loss in weight of the copper oxide gave the weight of the oxygen, and the weight of the water minus the weight of the oxygen gave the weight of the hydrogen present. It was found that 8 parts of oxygen combined with 1 part of hydrogen to form water.

Dumas in 1842, and other chemists later, by this and other methods have determined with great accuracy the quantities of hydrogen and oxygen combined in water. Fig. 57 shows

diagrammatically the apparatus used by Dumas. He made hydrogen from zinc and dilute sulphuric acid.

The U tubes, etc., contained :—

1. Broken glass moistened with lead nitrate solution to remove sulphuretted hydrogen.

2. Broken glass moistened with silver sulphate solution to absorb arseniuretted hydrogen and phosphoretted hydrogen.

3, 4, and 5. Caustic potash to absorb sulphur dioxide and carbon dioxide as well as some moisture.

6 and 7. Phosphorus pentoxide to absorb water vapour. The tubes were cooled in a freezing mixture.

8. Phosphorus pentoxide, weighed before and after each experiment to see whether the hydrogen passed into the bulb was absolutely dry.

9. Copper oxide. This bulb was heated.

10. Most of the water formed.

11. Solid caustic potash.

12. Phosphorus pentoxide ; the tube was placed in a freezing mixture.

13. Phosphorus pentoxide.

14. Phosphorus pentoxide ; placed at the end to prevent absorption of moisture from the air by the weighed tubes.

The loss of weight of the copper oxide bulb gave the weight of oxygen. The increase in weight of the bulb 10 and the tubes 11, 12, and 13 gave the weight of water formed.

Dumas found as the mean of a large number of experiments that 2 grams of hydrogen combine with 15.96 grams of oxygen.

Very exact experiments have been carried out recently by Lord Rayleigh and by Morley. Their results are very little different from those of Dumas.

Composition of water by volume

You have learnt that Cavendish proved that two volumes of hydrogen combine with one volume of oxygen to give water, and you have also learnt that water gives on electrolysis two volumes of hydrogen to one volume of oxygen, the acid present enabling the water to conduct electricity, and

remaining after the experiment in the same quantity as before the experiment.

The method used at the present day is due to Bunsen. Fig. 58 shows the apparatus employed.

A is a strong uniform glass tube with a millimetre scale etched on it. Through it, near the top, are sealed platinum wires, the ends of which inside the tube are separated by about a quarter of an inch.

B is a thermometer hung alongside **A**. The temperature is read by means of a telescope at a distance.

C is a mercury trough.

A is filled with mercury; a few drops of water are then put in and pure oxygen is introduced. The barometer and thermometer are read, and the levels of the mercury in the tube and in the trough are read by means of the telescope, so that the heat of the body may not influence the volume of the gas. The volume of oxygen at 0° C. and 760 mm. can then be calculated.

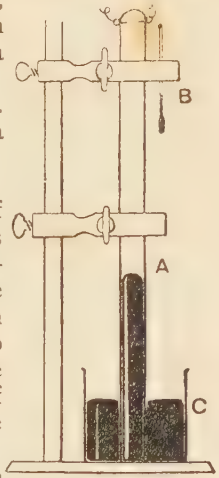


FIG. 58

Pure hydrogen, more than enough to completely combine with the oxygen, is next introduced, and its volume determined and calculated in the same way.

The eudiometer, as the tube **A** is called, is then pressed down tightly against a pad of india-rubber, and electric sparks are passed to ignite the gases. The pad is removed, the tube is allowed to cool, and the volume of the residual hydrogen is found in the same way as before.

The object of the addition of a few drops of water is to ensure that the gas is saturated with water vapour. The correction, for water vapour, for a gas at a known temperature can readily be made if the gas is saturated. If water had not been introduced, and dry oxygen and hydrogen had been used, only the hydrogen left after the explosion would have been moist, and even that possibly would not have been saturated.

Suppose that the volume of the oxygen reduced to 0° C. and

760 mm. was 14.7 volumes, the volume of the hydrogen added 98.9 volumes, and the volume of the residual hydrogen 69.5 volumes. The volume of hydrogen used up must have been $98.9 - 69.5 = 29.4$ volumes. Therefore 29.4 volumes of hydrogen combine with 14.7 volumes of oxygen. That is, 2 volumes of hydrogen combine with 1 volume of oxygen to form water.

Volume composition of steam

It is important to know the relation that exists between the volumes of oxygen and hydrogen combining together, and the volume of steam produced. In order to find this, the eudiometer, in which the explosion takes place, must be kept at a temperature above the boiling-point of water. Fig. 59 shows a suitable apparatus.

The eudiometer is marked off with three bands into three equal divisions, and surrounded by a glass jacket into which the vapour of amyl alcohol, boiling at 130° C., can be driven. The amyl alcohol vapour keeps the whole eudiometer at a constant temperature of 130° C. The vapour is led away from the bottom of the jacket and condensed.

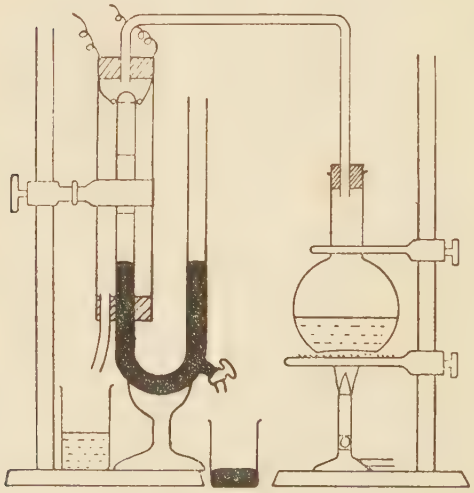


FIG. 59

A mixture of hydrogen and oxygen, in the proportions of 2 volumes to 1 volume, is introduced into the eudiometer until the mixed gases fill the marked-off volumes, when the tem-

perature is 130° C. and the mercury is at the same level in both limbs. The open limb is next completely filled with mercury and the thumb pressed tightly on the open end to prevent ejection of mercury when the spark is passed. A spark from a Ruhmkorff coil is then passed.

Next, the level of the mercury is adjusted until it is the same in both tubes. It is found that the volume of the steam is two-thirds of that of the mixed gases.

Two volumes of hydrogen have combined with 1 volume of oxygen to give 2 volumes of steam. This is in accordance with Gay Lussac's Law of Volumes (*q.v.*).

Formula for water

Let us now find the formula of water. The composition of water by weight tells us that nearly 8 parts of oxygen combine with 1 part of hydrogen. The atomic weight of oxygen is 16 and of hydrogen 1. The density of steam compared with that of hydrogen is 9.

				Number of atoms
Hydrogen	=	$\frac{1}{1}$	=	1
Oxygen	=		=	0.5

$\therefore$ 1 atom of oxygen combines with 2 atoms of hydrogen.

There may, however, be 2 or 3 or 4 atoms of oxygen combined with 4 or 6 or 8 atoms of hydrogen respectively.

$\therefore$ The formula must be $(H_2O)_x$ where x is some small whole number.

But the density of steam is 9.

$\therefore$ The molecular weight of steam is 18.

$\therefore$ $(H_2O)_x = 18$.

$\therefore$ $(2+16)_x = 18$.

$\therefore$ $x = 1$.

$\therefore$ The formula for water is H_2O.

The combining volumes of oxygen and hydrogen also readily indicate the formula if we know that the molecules of hydrogen and oxygen each contain 2 atoms.

Thus 1 volume of oxygen contains n molecules $= 2n$ atoms of oxygen.

2 volumes of hydrogen contain $2n$ molecules $= 4n$ atoms of hydrogen.

$\therefore$ n atoms of oxygen combine with $2n$ atoms of hydrogen.
$\therefore$ The formula is $(H_2O)_x$.
But the density of steam is 9.
$\therefore$ The molecular weight of steam is 18.
$\therefore$ $(H_2O)_x = 18$. $\therefore$ $(2+16)_x = 18$. $\therefore$ $x = 1$.
$\therefore$ The formula is H_2O.

HYDROGEN PEROXIDE, H_2O_2. Molecular weight = 34

Occurrence—In very small quantities in the atmosphere, rain, and snow.

Preparation—Action of dilute acids on barium peroxide, BaO_2. The acid should be in excess, because barium peroxide reacts with hydrogen peroxide, giving barium hydroxide, $Ba(OH)_2$, and oxygen.

$$\underset{\text{Barium peroxide}}{BaO_2} + 2HCl = \underset{\text{Barium chloride}}{BaCl_2} + H_2O_2$$

If a pure solution of hydrogen peroxide is wanted, the excess of hydrochloric acid and barium chloride is removed by addition of silver sulphate, Ag_2SO_4.

$$2HCl + \underset{\text{Silver sulphate}}{Ag_2SO_4} = \underset{\text{Silver chloride}}{2AgCl} + \underset{\text{Sulphuric acid}}{H_2SO_4}$$

$$BaCl_2 + Ag_2SO_4 = \underset{\text{Barium sulphate}}{BaSO_4} + 2AgCl$$

The sulphuric acid and excess of silver sulphate are removed by addition of excess of baryta water.

$$Ag_2SO_4 + \underset{\text{Baryta water}}{Ba(OH)_2} = \underset{\text{Silver oxide}}{Ag_2O} + H_2O + BaSO_4$$

$$H_2SO_4 + Ba(OH)_2 = BaSO_4 + 2H_2O$$

The excess of baryta water is removed by passing carbon dioxide through the solution.

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O$$

The solution is then filtered from the insoluble silver chloride, barium sulphate, silver oxide, and barium carbonate, and concentrated by evaporating *in vacuo* over sulphuric acid. In this way pure hydrogen peroxide is obtained as a colourless, odourless, syrupy liquid.

Properties—The solution of hydrogen peroxide obtained by the above method is colourless and without smell.

On warming, the solution of hydrogen peroxide is readily split up into H_2O and oxygen. $2H_2O_2 = 2H_2O + O_2$.

Hydrogen peroxide ought, therefore, to be an oxidising agent. It is. It readily oxidises black lead sulphide to white lead sulphate.

$$\underset{\text{Lead sulphide}}{PbS} + 4H_2O_2 = \underset{\text{Lead sulphate}}{PbSO_4} + 4H_2O$$

This action is made use of in restoring pictures. The white lead paint in the pictures becomes tarnished and blackened by the sulphuretted hydrogen in the air of towns. The black lead sulphide can be converted to white lead sulphate by treating the picture with hydrogen peroxide.

Hydrogen peroxide is a good bleaching agent for vegetable colours, owing to the ease with which it gives up half of its oxygen. This oxygen forms white or colourless products with the colouring matter. Hydrogen peroxide will bleach hair, the teeth, ivory, and indigo.

Although hydrogen peroxide is an oxidising agent, it has the power of reducing the proportion of oxygen in a number of compounds which contain oxygen loosely combined. This is probably owing to greater attraction between oxygen atoms themselves than between the oxygen atoms and the compound containing them.

Thus acidified potassium permanganate is decolorised by hydrogen peroxide and oxygen is given off.

$$\underset{\text{Potassium permanganate}}{2KMnO_4} + 5H_2O_2 + 3H_2SO_4 = \underset{\text{Potassium sulphate}}{K_2SO_4} + \underset{\text{Manganese sulphate}}{2MnSO_4} + 5O_2 + 8H_2O$$

Five oxygen atoms come from the potassium permanganate and five from the hydrogen peroxide.

Again, silver oxide Ag_2O is reduced to metal by hydrogen peroxide.

$$Ag_2O + H_2O_2 = 2Ag + O_2 + H_2O$$

Hydrogen peroxide is readily detected in solution by the addition of acidified potassium bichromate solution and ether. When the mixture is shaken, the ether becomes deep blue.

PRACTICAL EXERCISES

(1) Find the solubility of common salt at the temperature of the laboratory.

(2) Find the number of molecules of water of crystallisation in zinc sulphate and in barium chloride.

(3) Find the volume of oxygen, measured at 0° C. and 760 mm., which is evolved on heating from 1 c.c. of the given solution of hydrogen peroxide.

(4) Titrate the same solution of hydrogen peroxide with standard

potassium permanganate solution. It may be necessary to dilute the solution before titration.

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

Calculate the weight of H_2O_2 in 1 c.c. of the undiluted solution, and calculate the volume of oxygen which would be evolved on heating 1 c.c. of the solution.

Compare your result with that obtained in (3).

CHAPTER XII

OXYGEN—OXIDES—OXIDATION AND REDUCTION—OZONE

Exp. 77—To prepare oxygen and examine its properties

Directions—Use 3 parts of powdered potassium chlorate and 1 part of manganese dioxide. Make a list of the properties of oxygen.

Examine the action on litmus of the products of combustion of ordinary substances in oxygen.

Exp. 78*—To prove that the manganese dioxide used in the preparation of oxygen is unaltered in the reaction

Directions—Weigh with the lid a crucible containing about 3 grams of powdered potassium chlorate. Into the weighed crucible introduce about 1 gram of dry manganese dioxide and weigh again. Now mix the contents of the crucible thoroughly with a clean knife blade or spatula, and carefully detach any particles adhering to the blade or spatula.

Next gently heat the crucible with the lid slightly displaced. Gradually raise the temperature until all the oxygen has come off. Allow to cool. Treat the black residue with small quantities of hot water until all soluble matter has been removed, and pour through a filter paper, which has been previously dried and weighed, the solutions thus obtained. Repeat until all the insoluble residue is on the paper. Take great care to avoid any loss of insoluble matter. Finally, wash the residue on the filter paper several times with hot water. Dry and weigh.

Is the manganese dioxide left on the paper equal in weight to that used in the first place? If so, it is highly probable that the manganese dioxide is unchanged.

* The manganese dioxide used in this experiment should previously have been freed from soluble matter by treatment with water.

Exp. 79—To find the percentage of oxygen in potassium chlorate, and the weight of a litre of dry oxygen at 0° C. and 760 mm.

Directions—Weigh accurately about .3 gram of potassium chlorate into a hard glass tube sealed at one end. Fit the tube near the middle with a loose plug of dry asbestos. Weigh the whole. Connect the tube with an apparatus for measuring the volume of oxygen produced, and heat the potassium chlorate strongly until no more oxygen is evolved. Allow to cool, and again weigh. Correct the volume of oxygen for temperature and pressure.

Calculate (1) the percentage of oxygen present in the potassium chlorate and (2) the weight of a litre of oxygen at 0° C. and 760 mm. A litre of hydrogen at N.T.P. weighs .09 gram. What is the density of oxygen?

Exp. 80—To find out whether the given oxides are acidic oxides, basic oxides, or peroxides

Directions—(1) Shake up a little of the oxide with water in a test-tube, filter if necessary, and try the effect of the solution on litmus, sodium carbonate, and zinc.

Solutions of acidic oxides act like acids; basic oxides, if soluble, turn purple litmus blue.

(2) Heat some of the oxide with strong hydrochloric acid and test for chlorine by smell, colour, and starch iodide papers.

Evolution of chlorine indicates the presence of a peroxide.

(3) Heat some of the oxide with strong sulphuric acid. Test for oxygen with a glowing splinter.

Evolution of oxygen indicates the presence of peroxide.

(4) If the oxide has no effect on litmus and it is insoluble in water, put excess of it into a small quantity of dilute hydrochloric acid, warm for some time, filter, and evaporate to see if a salt has been formed. If no salt is obtained with hydrochloric acid, try dilute nitric acid, and then dilute sulphuric acid.

Basic oxides form salts with dilute acids.

Write a full account of your results, and draw conclusions from each test.

Exp. 81—To find out if the substances provided are oxidising or reducing agents

Directions—Try the following tests for oxidising agents:—

(1) Acidify potassium iodide solution with dilute sulphuric acid, and gently warm the mixture with the substance.

Iodine set free indicates an oxidising agent. The iodine is recognised by the deep red colour it gives to the solution, and the violet vapour it gives when the solution is boiled. If much iodine is set free, a black precipitate of solid iodine is formed. Iodine also gives a deep blue colour with cold starch paste.

This test always acts, even with weak oxidising agents.

(2) Add a solution of sulphuretted hydrogen to a solution of the substance and warm the mixture.

A white precipitate of sulphur indicates the presence of an oxidising agent.

This test does not act with all oxidising agents.

Next try the following tests for reducing agents :—

(*a*) Warm with a mixture of ferric chloride and freshly made potassium ferricyanide solution.

A deep blue precipitate of Prussian blue indicates that a reducing agent is present.

This test is very delicate.

(*b*) Warm a solution of the substance with a few drops of potassium permanganate solution which has been acidified with dilute sulphuric acid.

If the permanganate is decolorised, a reducing agent is present.

(*c*) Warm with an acidified solution of potassium bichromate.

If the bichromate solution is reduced to a green solution of chromium salt, a reducing agent is present.

OXYGEN. Symbol, O

History—Oxygen was discovered in 1774 by Priestley, who obtained it by heating oxide of mercury with a burning-glass. Scheele, a Swedish chemist, had obtained oxygen in 1773 by heating nitre and other substances, but his work was not published until 1775.

Lavoisier gave oxygen its name (ὀξύς = acid, γεννάω = I produce). He believed that all acids contained oxygen, a belief since proved to be wrong.

Occurrence—Oxygen occurs in the free state in air, of which it forms one-fifth by volume. Combined with other elements

it constitutes about one-half by weight of the crust of the earth and eight-ninths by weight of the sea.

Formation — (1) In the laboratory it is prepared by heating a mixture of powdered potassium chlorate (3 parts) and manganese dioxide (1 part) in a hard glass flask. The manganese dioxide causes the potassium chlorate to give up its oxygen at a lower temperature and more regularly. The manganese dioxide remains unchanged.

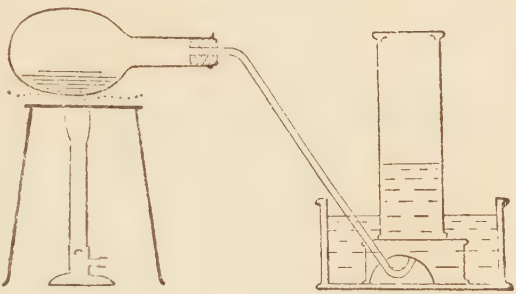


FIG. 60

$$2KClO_3 = 2KCl + 3O_2$$

Potassium chlorate — Potassium chloride

A substance which helps a chemical change and is itself unchanged at the end of the reaction is called a **catalytic agent.** It is supposed that the manganese dioxide acts in the following manner :—

(*a*) $2MnO_2 + 2KClO_3 = 2KMnO_4 + Cl_2 + O_2$

Manganese dioxide — Potassium permanganate

The potassium permanganate then breaks up.

(*b*) $2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$

Potassium manganate

The potassium manganate reacts with the chlorine formed in (*a*).

(*c*) $K_2MnO_4 + Cl_2 = 2KCl + MnO_2 + O_2$

If the same quantities of substances present on opposite sides of the three equations taken together are cancelled out, the remaining substances give the ordinary equation $2KClO_3 = 2KCl + 3O_2$.

The evidence for the above view of the action of the manganese dioxide is (1) the presence of traces of chlorine during the reaction, (2) the red colour of the potassium permanganate which is sometimes seen during the reaction.

(2) Oxygen may also be obtained by heating mercuric oxide, peroxides, and other substances rich in oxygen.

Thus $2HgO = 2Hg + O_2$

$3MnO_2 = Mn_3O_4 + O_2$

Red manganese oxide

A very high temperature is necessary.

$$2PbO_2 = 2PbO + O_2$$
Lead peroxide — Lead monoxide

$$2BaO_2 = 2BaO + O_2$$
Barium dioxide — Baryta

$$2KNO_3 = 2KNO_2 + O_2$$
Potassium nitrate — Potassium nitrite

(3) Oxygen is also obtained by heating peroxides with strong sulphuric acid, or potassium permanganate and potassium bichromate with dilute sulphuric acid.

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$$
$$4KMnO_4 + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2$$
$$2K_2Cr_2O_7 + 8H_2SO_4 = 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$
Potassium bichromate — Chromium sulphate

(4) *Manufacture of oxygen from the air*

Oxygen was until recently made extensively from the air by Brin's process. It has been found that oxygen is taken up by baryta, BaO, at a temperature of about 700° to form barium dioxide, BaO_2.

$$2BaO + O_2 = 2BaO_2$$

At the same temperature, but under reduced pressure, the barium dioxide readily gives up oxygen and is converted again to baryta.

Air freed from water vapour and carbon dioxide is pumped for 15 minutes into a large number of retorts containing baryta heated to 700° C. The pumps are then automatically reversed, and the pressure thereby reduced until it is equal to about 660 mm. of mercury, at which pressure barium peroxide gives up one of its oxygen atoms. The oxygen is then drawn away by the pumps and driven into a gas holder. The first portions of oxygen obtained are mixed with air. The automatic gear is so arranged that these portions are sent into the air and only the pure oxygen sent to the gas holder.

Oxygen is now made on the large scale by liquefying air, allowing the low-boiling liquid nitrogen to evaporate, and sending into the market the oxygen obtained from the higher-boiling liquid oxygen.

Properties—Atomic weight = 16. Molecular weight = 32. Density towards hydrogen = 16. Density relative to air = 1.1. Solubility = .041 c.c. in 1 c.c. of water at 0° C. Boiling-point = −181° C.

Oxygen is a colourless gas with no smell or taste. It is somewhat heavier than air. It is only slightly soluble in water. Fish, however, depend for their breathing on the oxygen dissolved in water.

Oxygen is chemically an active gas. Phosphorus, sodium, and even iron are converted into oxides if exposed to the air or oxygen. Sulphur, phosphorus, charcoal, iron, sodium, magnesium burn more brightly in this gas than in air, forming sulphur dioxide SO_2, phosphorus pentoxide P_4O_{10}, carbon dioxide CO_2, magnetic oxide of iron Fe_3O_4, sodium dioxide Na_2O_2, and magnesium oxide MgO respectively.

None of these substances will, however, burn in perfectly dry oxygen. The presence of the smallest trace of water vapour allows the action to take place, but the method of the action of the water vapour is not properly understood.

Oxygen supports the breathing of animals. But if pure oxygen be breathed for more than a short time, bad results ensue. It is sometimes administered by doctors to patients who are suffering from pneumonia, in which disease the lungs do not provide sufficient oxygen for the proper oxidation of the blood.

For an account of the breathing of animals and plants see page 57.

Oxygen can be liquefied at $-113°$ C. by a pressure of about 50 atmospheres. Liquid oxygen is bluish in colour and is strongly magnetic. It expands, when heated, even more rapidly than a gas. It is less active than the gas; for example, it has no action on phosphorus, sodium, or potassium.

Test for oxygen—With nitric oxide, NO, it produces a red gas, nitrogen peroxide, NO_2 or N_2O_4.

OXIDES

Oxides may be divided into four classes: (1) Acidic oxides; (2) Basic oxides; (3) Peroxides; (4) Neutral oxides.

Acidic oxides are mostly oxides of non-metals, but some of the higher oxides of the metals are acidic.

Thus, sulphur dioxide SO_2, sulphur trioxide SO_3, nitrogen pentoxide N_2O_5, phosphorous and phosphoric oxides P_4O_6 and P_4O_{10}, carbon dioxide CO_2 are acidic oxides of non-metals.

Chromic anhydride CrO_3, manganese heptoxide Mn_2O_7 are acidic oxides of metals.

There is no general method of making these oxides, but most of the non-metallic acidic oxides can be made by heating the non-metal in oxygen.

Acidic oxides are usually soluble in water. The solution in water will redden blue litmus, react with sodium carbonate, giving off carbon dioxide, and in many cases react with zinc to give hydrogen.

Basic oxides are oxides of metals.

They may be prepared in a number of ways.

(1) Heat the metal in a stream of oxygen.

$$2Cu + O_2 = 2CuO \quad \text{Cupric oxide}$$

$$2Pb + O_2 = 2PbO \quad \text{Lead monoxide}$$

(2) Heat the hydroxide of the metal. The hydroxide can usually be precipitated from a solution of a salt of the metal by addition of caustic soda solution.

$$2Fe(OH)_3 = \underset{\text{Ferric oxide}}{Fe_2O_3} + 3H_2O$$

$$Zn(OH)_2 = \underset{\text{Zinc oxide}}{ZnO} + H_2O$$

(3) Heat the carbonate of the metal.

$$MgCO_3 = \underset{\text{Magnesium oxide}}{Mgo} + CO_2$$

$$CaCO_3 = \underset{\text{Calcium oxide or lime}}{CaO} + CO_2$$

(4) Heat the nitrate of the metal.

$$2Ba(NO_3)_2 = 2BaO + 4NO_2 + O_2$$

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

Some metals, such as iron and copper, form two oxides, both of which are basic, *e.g.* ferrous oxide FeO, ferric oxide Fe_2O_3, cuprous oxide Cu_2O, cupric oxide CuO.

The basic oxides, when soluble in water, turn red litmus blue. They give no effervescence with sodium carbonate or zinc. They will usually dissolve in acids, neutralising them and forming salts and water.

Thus $ZnO + H_2SO_4 = H_2O + ZnSO_4$ Zinc sulphate

$PbO + 2HNO_3 = H_2O + Pb(NO_3)_2$ Lead nitrate

Peroxides are mainly oxides of metals containing more oxygen than the basic oxides of the same metals.

Examples—Lead peroxide PbO_2, manganese dioxide MnO_2, barium peroxide BaO_2, sodium peroxide Na_2O_2.

Compare these with the basic oxides,

$$PbO, MnO, BaO, Na_2O$$

Each peroxide is made in its own special way.

The peroxides of the metals (1) when heated alone give off oxygen; (2) when heated with strong hydrochloric acid give off chlorine; (3) when heated with strong sulphuric acid give off oxygen.

Hydrogen-peroxide H_2O_2 and chlorine peroxide ClO_2 are examples of peroxides of non-metals. They give off oxygen when heated.

(1) Heat $3MnO_2 = Mn_3O_4 + O_2$, $2BaO_2 = 2BaO + O_2$

(2) Heat with strong hydrochloric acid

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$$
$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$

(3) Heat with strong sulphuric acid

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$$

Neutral oxides—This class includes such oxides as carbon monoxide CO, nitrous oxide N_2O, water H_2O. These oxides have no effect on litmus, and give no reaction with hydrochloric acid, sulphuric acid, or sodium carbonate.

Compound oxides—Oxides such as red lead Pb_3O_4 and magnetic oxide of iron Fe_3O_4 behave towards acids as if they were composed of two oxides combined together. Thus red lead acts as if it had the composition $PbO_2.2PbO$, and the magnetic oxide of iron as if it had the composition $FeO.Fe_2O_3$. Such oxides may be called *compound oxides*.

Amphoteric oxides—Some oxides of metals show both acidic and basic properties. Aluminium oxide, Al_2O_3, which has not been heated strongly, will neutralise hydrochloric acid giving the salt aluminium chloride, and will also react with caustic soda giving sodium aluminate.

$$Al_2O_3 + 6HCl = 2AlCl_3 + 3H_2O$$
$$Al_2O_3 + 6NaOH = 2Na_3AlO_3 + 3H_2O$$

It is, therefore, both acidic and basic, and is said to be *amphoteric*. Stannic oxide, SnO_2, lead peroxide, PbO_2, and zinc oxide, ZnO, are also amphoteric oxides.

OXIDATION AND REDUCTION

Oxidation of a substance does not necessarily mean the addition of oxygen.

A chemical change which brings about an increase in the proportion of the electro-negative or non-metallic part of a molecule, or which causes a decrease in the proportion of the electro-positive or metallic part of a molecule, is known as a case of **oxidation.**

Increase in the electro-positive part or decrease in the electro-negative part of a molecule constitutes **reduction.** Reduction is therefore the converse of oxidation.

When magnesium is burnt in air, the magnesium is *oxidised*, for oxygen has been added to it. $2Mg + O_2 = 2MgO$.

When chlorine is passed over heated ferrous chloride, chlorine, a non-metallic element, is added and the ferrous chloride is *oxidised* to ferric chloride. $2FeCl_2 + Cl_2 = 2FeCl_3$.

If ferric sulphate solution is treated with zinc and dilute sulphuric acid, the nascent hydrogen produced by the action of the zinc and dilute sulphuric acid *reduces* the ferric sulphate (Fe : SO_4 as 2 : 3) to ferrous sulphate (Fe : SO_4 as 2 : 2).

$$Fe_2(SO_4)_3 + 2H = 2FeSO_4 + H_2SO_4$$

Again, if carbon monoxide is passed over strongly heated ferric oxide, the ferric oxide is *reduced* to metallic iron, and the carbon monoxide is oxidised to carbon dioxide.

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$

Oxidation and reduction must always take place in the same reaction. If a compound is oxidised, the compound reacting with it must be reduced. Thus stannous chloride solution reduces mercuric chloride to mercurous chloride, and is itself oxidised to stannic chloride.

$SnCl_2$	+	$2HgCl_2$	=	$SnCl_4$	+	Hg_2Cl_2
Stannous chloride		Mercuric chloride		Stannic chloride		Mercurous chloride

Exceptions must be made to the above definition of oxidation. In the examples given below, oxidation has not taken place, although in (1) the proportion of non-metallic elements to barium has been increased, and in (2) the proportion of non-metallic elements has been increased from 71 of chlorine to 124 of (NO_3).

(1)	BaO	+	2HCl	=	$BaCl_2$	+	H_2O
	Barium oxide				Barium chloride		

(2) $FeCl_2$ + $2AgNO_3$ = $Fe(NO_3)_2$ + $2AgCl$
Ferrous chloride — Silver nitrate — Ferrous nitrate — Silver chloride

In these, and in many similar cases, the electro-negative element or group of elements is changed to a completely different element or group of elements. There has been no addition to, or subtraction from, the group; there has been simply a substitution of one element or group of elements for another.

In these changes (1A) and (2A), true oxidation has taken place. In (1A) the oxygen combined with the barium has been increased, and in (2A) the chlorine combined with the iron has been increased.

(1A) $2BaO + O_2 = 2BaO_2$ Barium peroxide
(2A) $FeCl_2 + Cl$ (nascent) $= FeCl_3$ Ferric chloride

Oxygen, nitric acid, chlorine, potassium chlorate, bleaching powder, chromic anhydride, and potassium permanganate are examples of common oxidising agents.

Hydrogen, carbon, carbon monoxide, sulphur dioxide, sulphuretted hydrogen, ferrous sulphate solution, and stannous chloride solution are examples of reducing agents.

Hydrogen peroxide acts both as an oxidising agent and a reducing agent. It sets free the iodine from acidified potassium iodide, and it also decolorises acidified potassium permanganate solution.

Oxidation. $2HI + H_2O_2 = 2H_2O + I_2$
Hydriodic acid

Reduction.

$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = 5O_2 + 8H_2O + K_2SO_4 + 2MnSO_4$
Potassium permanganate — Potassium sulphate — Manganese sulphate

OZONE. Symbol, O_3. Molecular weight = 48. Density = 24.

Formation—(1) Perhaps the best apparatus for the preparation of ozone is that shown in Fig. 61.

A tube **A** is sealed into a larger tube **B,** so that there is an annular space between the tubes. Two narrow tubes **C** and **D** are let into **B** in the positions shown. **E** and **F** are wires from a Rhumkorff coil dipping into dilute sulphuric acid Oxygen is slowly passed through **C,** and the coil is set going.

The oxygen between the two tubes is subjected to a strong electric strain. No electric sparks actually pass between **A** and **B**. This discharge of electricity is known as the silent discharge. The oxygen passing out at **D** may contain 5 or 6 per cent. of ozone.

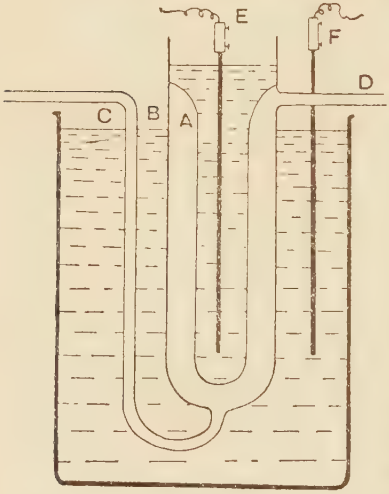


FIG. 61

(2) The oxygen in air may be ozonised by partly immersing a stick of phosphorus in water in a glass cylinder. After a short time the air in the cylinder will turn starch iodide papers blue.

(3) Fairly pure ozone can be obtained from the anode when acidulated water is electrolysed, if the platinum anode is not larger than a pin's head and a high current density is used.

Properties—Ozone (ὄζω, a smell) is a colourless gas with a peculiar smell somewhat resembling very dilute chlorine. It is slightly soluble in water. It is a very powerful oxidiser; if ozonised oxygen is passed through an india-rubber tube, the india-rubber quickly decays. Ozone bleaches dilute indigo solution and other vegetable colouring matters. It attacks most metals readily, forming oxides. Even mercury is attacked by it. Slight traces of ozone dull the surface of mercury owing to the formation of an oxide, and the mercury, after contact with the ozone, leaves "tails" when moved about in a glass vessel. Lead sulphide is rapidly converted by ozone into lead sulphate (*cf.* hydrogen peroxide).

$$\underset{\text{(Black)}}{PbS} + 4O_3 = \underset{\text{(White)}}{PbSO_4} + 4O_2$$

Ozone readily liberates iodine from potassium iodide. If a piece of paper is dipped into starch solution containing some potassium iodide and afterwards exposed to ozone, the paper is turned blue from the action of the starch with the iodine liberated.

$$2KI + O_3 + H_2O = 2KOH + I_2 + O_2$$

If ozone be heated to 250° to 300° C., it is converted to oxygen. $2O_3 = 3O_2$

Ozone is decomposed by oxides of magnesium, copper, and silver. The oxides are unchanged, and therefore their action is catalytic. Possibly the action consists of a reduction of the oxide and then an oxidation of the metal. Thus—

$$Ag_2O + O_3 = 2Ag + 2O_2$$
$$2Ag + O_3 = Ag_2O + O_2$$

Silver oxide

Ozone has been condensed by extreme cold to a liquid which has a deep blue colour. The liquid is very explosive, and boils between − 119° C. and − 125° C.

The presence of ozone in country air and in sea air is believed to conduce to health. Ozone destroys germs and unwholesome organic matter in air, and consequently ozonised air is now used for the ventilation of tube railways.

Composition of ozone

From its method of formation and from its conversion to oxygen on being heated to 300° C., it is obvious that ozone contains no other element than oxygen.

When oxygen is ozonised it contracts, and when the tube or vessel containing the ozonised oxygen is heated to 300° C. and then allowed to cool, the gas returns to its original volume. The relation of the volume of the ozone to that of the oxygen composing the ozone was found by Soret. He opened a tube of ozonised oxygen under turpentine, a liquid which dissolves ozone but not oxygen, and so found the volume of the ozone. Another portion of the same ozonised oxygen he passed through a strongly heated tube packed with broken glass. The volume of the oxygen escaping from the tube he measured. The increase in volume represented the increase in volume of the ozone present when it was converted into oxygen. He found that for equal volumes of ozonised oxygen the volume absorbed by the turpentine was twice the increase in

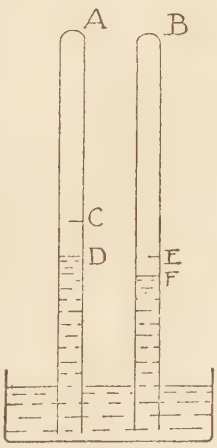


FIG. 62

volume when the ozonised oxygen was converted to oxygen. Soret's method may be understood better after a consideration of Fig. 62. *The figure does not represent apparatus that could actually be used. It merely illustrates Soret's results.*

Let **A** and **B** represent two tubes containing equal volumes of ozonised oxygen. Let turpentine be introduced into **A**. The contraction **CD** represents the volume of the ozone in the ozonised oxygen. Let the tube **B** be heated sufficiently strongly to convert the ozone into oxygen. Let the expansion after the tube is cold be **EF**. Then **EF** represents the expansion of a volume, **CD**, of ozone when it is converted into oxygen.

$$\mathbf{CD} = 2 \times \mathbf{EF} \quad \text{(Soret's result)}$$

If **EF** is 1 volume, then **CD** is 2 volumes. Therefore 2 volumes of ozone when heated give 3 volumes of oxygen.

$\therefore$ 2 molecules of ozone give 3 molecules of oxygen (Avogadro's Law). But 3 molecules of oxygen contain 6 atoms.

$\therefore$ 2 molecules of ozone contain 6 atoms of oxygen.

$\therefore$ The formula of ozone is O_3.

Soret also found the density of ozone by comparing its rate of diffusion with that of chlorine. He found that 1 volume of ozone diffuses as quickly as .8376 volume of chlorine.

$$\therefore \frac{1}{.8376} = \frac{\sqrt{\text{Density of chlorine}}}{\sqrt{\text{Density of ozone}}} \quad \text{(Graham's Law)}$$

$$\therefore \frac{1}{.8376} = \frac{\sqrt{35.11}}{\sqrt{x}}$$

$$\therefore x = 24.8$$

Therefore the molecular weight of ozone is 49.6 But the weight of 3 atoms of oxygen is 48. Experimental errors will account for the difference, 1.6. Therefore the formula of ozone is O_3.

Allotropy

Oxygen and ozone are two forms of the same element. They differ considerably in properties. Oxygen has no smell; ozone has a strong smell. Oxygen will not attack mercury or india-rubber at ordinary temperature, has no effect on starch iodide papers, and will not bleach indigo; whereas ozone tarnishes mercury, destroys india-rubber, turns starch iodide paper blue, and bleaches indigo. This great difference is caused solely by the difference in the number of atoms in the molecule: O_2 = oxygen, O_3 = ozone.

The phenomenon of the existence of more than one form of the same element is known as **allotropy.** The different forms are known as *allotropic forms* or *allotropic modifications* of the element. Other elements besides oxygen exhibit allotropy. For example, carbon exists in three distinct forms, diamond, graphite, and charcoal; sulphur in four forms,

rhombic, prismatic, plastic, and amorphous ; and phosphorus in two forms, yellow and red.

In each of these cases the difference in properties of the different forms is most probably due to either a difference of the number of atoms in the molecule, or to a difference in the arrangement of the atoms in the molecule ; possibly both number and arrangement may play their part. Mere difference in crystalline form, or absence of crystalline form, might easily be accounted for by a difference in the arrangement of the molecules themselves. Thus one may regard crystalline diamond as a structure of molecules built up on a regular plan (like a brick wall), and charcoal as a number of molecules joined together in a manner lacking all regular arrangement (like a heap of bricks).

PRACTICAL EXERCISES

(1) From the metals—copper, lead, magnesium, zinc, iron, tin and aluminium prepare specimens of the common oxides of the metals.

(2) From the salts—barium nitrate, magnesium carbonate, zinc sulphate, ferric chloride, chromium sulphate, lead acetate, and cupric chloride prepare specimens of barium monoxide, magnesium oxide, zinc oxide, ferric oxide, chromium oxide, lead monoxide, and cupric oxide respectively.

CHAPTER XIII

ACIDS, BASES, AND SALTS

Exp. 82—To determine the properties common to acids

Directions—

(1) Try to make a solution of the acid in water.

(2) Taste a very weak solution of the acid. *Your master's permission should first be obtained, as some acids are strong poisons.*

(3) Test with litmus.

(4) Add a few drops of acid solution to sodium carbonate and test for carbon dioxide.

(5) Add a few c.c. of acid solution to metallic zinc. If no action takes place, warm. Test for hydrogen.

(6) To about 20 c.c. of acid, add, with constant stirring, caustic soda solution until a drop taken out has no effect on litmus paper. Then evaporate and try to get crystals of a salt.

Each of these tests should be tried with a number of acids. Make a list of properties common to acids.

Exp. 83—To determine the properties common to bases

Directions—

(1) Find out if all the bases provided are soluble in water.

(2) Taste a very weak solution of the base.

(3) Test with litmus.

(4) Add excess of solution of the base to a few c.c. of copper sulphate solution, and note whether a bluish precipitate of copper hydroxide is formed.

(5) Neutralise 20 c.c. of the solution of the base with hydrochloric acid and evaporate down to the crystallising point.

If the base is insoluble, warm excess of it with dilute hydrochloric, nitric, or sulphuric acid, filter and evaporate the filtrate to the crystallising point.

Is a salt produced in every case ?

Make a list of properties common to bases.

Exp. 84—To determine properties common to salts

Directions—Determine, by observation and experiment, the answers to the following questions :—

(1) Are all salts solid ?

(2) Are all salts crystalline ?

(3) Do all salts dissolve in water ?

(4) Are all salts neutral to litmus ?

(5) Are solutions of all soluble salts precipitated by caustic soda solution ?

(6) Do all salts react with hot, strong, sulphuric acid ? Where action takes place, note the obvious properties of the substances formed.

ACIDS

You have found that solutions of the oxides of non-metals are usually acidic (exceptions—carbon monoxide, nitrous oxide, and water), that is, they dissolve in water to form acids. Acids, you have discovered, are soluble in water, and their solutions are sour to the taste. They turn blue litmus red ; they react with sodium carbonate, giving carbon dioxide ; they sometimes react with zinc, giving hydrogen ; and they neutralise caustic soda, giving a salt and water.

Chemists at one time believed that all acids contained

oxygen, and that the oxygen was the acidifying principle in acids. It was thought that salts were combinations of oxides of non-metals with oxides of metals. Thus calcium sulphate was regarded as $CaO.SO_3$ instead of $CaSO_4$; magnesium carbonate as $MgO.CO_2$ instead of $MgCO_3$.

Sir Humphrey Davy, at the beginning of the nineteenth century, proved, however, that hydrochloric acid, HCl, contained no oxygen, and that the chlorine, which was then believed to contain oxygen, was an element. Since that time other acids, hydrobromic acid HBr, hydriodic acid HI, hydrofluoric acid HF, hydrocyanic acid HCN have also been shown to contain no oxygen.

All acids do contain hydrogen. Do not think, however, that all substances which contain hydrogen are acids. Water H_2O, marsh gas CH_4, benzene C_6H_6, caustic soda NaOH, alcohol C_2H_6O, and thousands of other substances contain hydrogen, but are not acids. The hydrogen only forms acids, or becomes acidic, when it is combined with certain non-metallic atoms or groups of atoms.

The term acid is very difficult to define. Some people say that *an acid is a salt of hydrogen*. That is arguing in a circle, because *salt* is defined through acid. Others say that an *acid is a compound of hydrogen with an electro-negative atom or group of atoms, which, when the hydrogen is partly or wholly replaceable by metals presented to it in the form of hydroxides, forms a salt and water.* This is again unsatisfactory because the term "salt" is introduced, and it is difficult to define the meaning of "electro-negarive atom or group of atoms." The difficulty may be avoided by stating that—

An **acid** *is a compound of the type* H_nX. *The hydrogen may be wholly or partly replaced by sodium when the acid is treated with caustic soda. The reaction with caustic soda must be possible in presence of a large quantity of water.*

$$H_nX + nNaOH = Na_nX + nH_2O$$

The last sentence is included to exclude zinc hydroxide, aluminium hydroxide, etc., substances which certainly are not acids, but which would be acids under the above definition with the last sentence omitted. The reaction between zinc hydroxide and caustic soda is—

$$Zn(OH)_2 + 2NaOH = Zn(ONa)_2 + 2H_2O$$

This reaction does not take place if the caustic soda it largely diluted. A true acid would combine with caustic soda even when very largely diluted.

Note.—An acid may be defined as a substance which, when dissolved in water, produces hydrogen ions. See Chapter XLVI.

Acids are said to be monobasic, dibasic, tribasic, etc., according as they contain one, two, three, etc., atoms of replaceable hydrogen in a molecule. **Basicity** of an acid may, therefore, be defined as *the number of hydrogen atoms in a molecule of the acid which are replaceable by sodium when the acid is treated with caustic soda.*

Thus hydrochloric acid HCl, nitric acid HNO_3, acetic acid $C_2H_4O_2$ are monobasic acids. It will be noticed that acetic acid contains four hydrogen atoms. Only one of these atoms is replaceable by metals.

$$C_2H_4O_2 + NaOH = C_2H_3O_2Na + H_2O$$

Sulphuric acid H_2SO_4, oxalic acid $C_2H_2O_4$, tartaric acid $C_4H_6O_6$ are examples of dibasic acids. Only two of the six hydrogen atoms in tartaric acid are replaceable by metals.

$$C_4H_6O_6 + 2KOH = C_4H_4O_6K_2 + 2H_2O$$

Phosphoric acid H_3PO_4 is a good example of a tribasic acid.

$$H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O$$

Preparation of acids

Acids may be prepared by—

(1) Dissolving acidic oxides in water.

$$\underset{\text{Sulphur trioxide}}{SO_3} + H_2O = \underset{\text{Sulphuric acid}}{H_2SO_4}$$

$$\underset{\text{Phosphorus pentoxide}}{P_4O_{10}} + 6H_2O = \underset{\text{Phosphoric acid}}{4H_3PO_4}$$

$$\underset{\text{Nitrogen pentoxide}}{N_2O_5} + H_2O = \underset{\text{Nitric acid}}{2HNO_3}$$

Acidic oxides, which dissolve in water with formation of acids, are known as *anhydrides.*

(2) Heating the salt of a volatile acid with a less volatile acid. Sulphuric acid boils at 338° C., and therefore can often be used as the less volatile acid.

$$\underset{\text{Potassium nitrate}}{2KNO_3} + H_2SO_4 = \underset{\text{Potassium sulphate}}{K_2SO_4n} + 2HNO_3$$

$$\underset{\text{Sodium chloride}}{2NaCl} + H_2SO_4 = \underset{\text{Sodium sulphate}}{Na_2SO_4} + 2HCl$$

(3) Treating a solution of the barium salt of an acid with the calculated quantity of dilute sulphuric acid. Insoluble barium sulphate is precipitated and a dilute solution of the acid is obtained on filtration. This method is very useful for the preparation of many weak acids, particularly those which are easily decomposed by heat.

$$\underset{\text{Barium chlorate}}{Ba(ClO_3)_2} + H_2SO_4 = BaSO_4 + \underset{\text{Chloric acid}}{2HClO_3}$$

(4) Passing sulphuretted hydrogen through water in which is dissolved or suspended the lead salt of the acid. Lead sulphide is precipitated and the acid is set free.

$$\underset{\text{Lead formate}}{Pb(HCO_2)_2} + H_2S = PbS + \underset{\text{Formic acid}}{2H_2CO_2}$$

BASES

We have seen that the lower oxides of the metals are basic.

A **base** *is generally an oxide or hydroxide of a metal which will neutralise an acid forming a neutral substance called a salt and water only.*

Thus copper oxide CuO, copper hydroxide $Cu(OH)_2$, sodium oxide Na_2O, and sodium hydroxide NaOH are bases.

$$Cu(OH)_2 + 2HNO_3 = Cu(NO_3)_2 + 2H_2O$$
$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

Ammonia NH_3, and a number of organic substances such as methylamine CH_3NH_2, and aniline $C_6H_5NH_2$, are also called bases. They form salts with acids, but give no water owing to their lack of the OH (hydroxyl) group.

$NH_3 + NHO_3 = NH_4NO_3$ Ammonium nitrate

$C_6H_5.NH_2 + HCl = C_6H_5.NH_2.HCl$ Aniline hydrochloride

Bases are frequently insoluble in water, *e.g.* ferric hydroxide $Fe(OH)_3$ and zinc hydroxide $Zn(OH)_2$. Caustic soda NaOH and caustic potash KOH are soluble in water.

When soluble in water, bases have a sharp caustic taste; they turn red litmus blue; they precipitate many of the hydroxides of metals from solution, and they neutralise acids to give salts and water.

$$\text{Thus } Cu(NO_3)_2 + 2KOH = \underset{\text{(insoluble)}}{Cu(OH)_2} + 2KNO_3$$
$$Al_2(SO_4)_3 + 6NaOH = 2\underset{\text{(insoluble)}}{Al(OH)_3} + 3Na_2SO_4$$

The name " base " (foundation) was originally given to these substances because that portion of a salt which was not driven off on heating strongly was regarded as the most important, and so was called the base. Most salts, when very strongly heated, leave behind a basic oxide.

$$2Cu(NO_3)_2 = 2CuO + 2NO_2 + O_2$$
$$Al_2(SO_4)_3 = Al_2O_3 + 3SO_3$$

Preparation of bases

(1) Methods used for preparation of oxides. See page 140.

(2) Treat the salt of a metal with a solution of another base. The insoluble hydroxide of the metal is usually precipitated.

$$\underset{\text{Ferrous chloride}}{FeCl_2} + 2KOH = \underset{\text{Ferrous hydroxide}}{Fe(OH)_2} + 2KCl$$

$$\underset{\text{Chromium Sulphate}}{Cr_2(SO_4)_3} + 6NaOH = \underset{\text{Chromium hydroxide}}{2Cr(OH)_3} + 3Na_2SO_4$$

SALTS

A **salt** *is a substance produced by the replacement of the whole or of part of the replaceable hydrogen of an acid by a metal.*

Nearly all salts are solid at ordinary temperature. Most of them are crystalline ; the majority are soluble in water, and many, but by no means all, are neutral to litmus. They may be divided into several classes—*normal salts, acid salts, basic salts, and double salts.*

(1) **Normal salts** are salts formed by the replacement by metals of all the replaceable hydrogen of the acid.

H_2SO_4 gives Na_2SO_4 = Normal sodium sulphate.

Acetic acid $C_2H_4O_2$ gives $C_2H_3O_2Na$ = Sodium acetate.

In sodium acetate three hydrogen atoms are still present. These, however, are not replaceable by metals. Therefore sodium acetate is a normal salt.

(2) **Acid salts** are salts formed by the replacement of part of the replaceable hydrogen of the acid.

Thus $$NaOH + H_2SO_4 = \underset{\text{Acid sodium sulphate}}{NaHSO_4} + H_2O$$

$$NaOH + H_3PO_4 = \underset{\text{Sodium dihydrogen phosphate}}{NaH_2PO_4} + H_2O$$

$$2NaOH + H_3PO_4 = \underset{\text{Disodium hydrogen phosphate}}{Na_2HPO_4} + 2H_2O$$

Both these phosphates are acid salts, for it is possible to replace all the hydrogen in phosphoric acid.

$$3NaOH + H_3PO_4 = \underset{\text{Normal sodium phosphate}}{Na_3PO_4} + 3H_2O$$

(3) **Basic salts** may be regarded as normal salts chemically combined with a base.

Thus $BiCl_3.Bi_2O_3$ is basic bismuth chloride or bismuth oxychloride. $BiCl_3$ is the normal salt.

$Pb(NO_3)_2.Pb(OH)_2$ is basic lead nitrate.

(4) **Double salts** are compounds of two normal salts.

Thus we may have salts containing one acid radicle and two metals, *e.g.* $K_2SO_4.Al_2(SO_4)_3.24H_2O$, ordinary alum.

Or we may have salts containing one metal and two acid radicles, *e.g.* $PbCl_2.PbS$, double salt of lead chloride and lead sulphide.

Preparation of salts

(1) Action of the acid on the metal, metallic oxide, hydroxide, or carbonate.

Thus—

$Zn + H_2SO_4 = H_2 + ZnSO_4$ Zinc sulphate

$CaO + 2HCl = H_2O + CaCl_2$ Calcium chloride

$2Fe(OH)_3 + 3H_2SO_4 = 6H_2O + Fe_2(SO_4)_3$ Ferric sulphate

$MgCO_3 + 2HNO_3 = CO_2 + H_2O + Mg(NO_3)_2$ Magnesium nitrate

(2) Double decomposition of salts.

The salts should be so selected that the products can readily be separated from one another (*a*) by filtration, owing to the insolubility of one of them ; or (*b*) by crystallisation, owing to difference of solubility.

(a) $\underset{\text{Barium chloride}}{BaCl_2} + \underset{\text{Sodium sulphate}}{Na_2SO_4} = \underset{\text{Barium sulphate (insoluble)}}{BaSO_4} + \underset{\text{Sodium chloride (soluble)}}{2NaCl}$

Filter from the insoluble barium sulphate.

(*b*) $NaNO_3$ + KCl = NaCl + KNO_3
Sodium nitrate — Potassium chloride — Sodium chloride — Potassium nitrate

The sodium chloride is not very soluble at temperatures near the boiling-point of the solution, whereas potassium nitrate is very soluble. By boiling down the solution and skimming off the crystals of sodium chloride as they form, a partial separation may be effected. Recrystallisation will further purify the salts obtained.

(3) Direct union of a metal and non-metal.

$2Na + Cl_2 = 2NaCl$
$Hg + I_2 = HgI_2$
Mercury — Mercuric iodide

Acid salts may generally be prepared by the action of the calculated quantity of acid on the normal salt.

$Na_2CO_3 + \underbrace{CO_2+H_2O}_{\text{Carbonic acid}} = 2NaHCO_3$
Sodium hydrogen carbonate

$Na_2SO_4 + H_2SO_4 = 2NaHSO_4$
Sodium hydrogen sulphate

Sometimes acid salts are produced by the neutralisation of bases with acids.

$2NaOH + H_3PO_4 = Na_2HPO_4 + 2H_2O$
Acid sodium phosphate (slightly alkaline to litmus)

Double salts—Most salts can be made by mixing together solutions of the calculated quantities of the two salts and evaporating until the double salt crystallises out.

$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O = K_2SO_4.Al_2(SO_4)_3.24H_2O$
Potassium sulphate — Aluminium sulphate — Potash alum

PRACTICAL EXERCISES

(1) Prepare specimens of acids from the following salts : (*a*) sodium nitrate, (*b*) potassium iodide, (*c*) lead oxalate.

(2) Prepare basic oxides from ferrous hydroxide, magnesium carbonate, lead nitrate.

(3) Prepare specimens of copper hydroxide and ferric hydroxide from copper sulphate and ferric chloride respectively.

Caution—Copper hydroxide must not be heated with caustic soda solution, owing to the ease with which it loses part of its combined water. Wash thoroughly and dry by pressing between pieces of blotting paper.

(4) (*a*) From metallic copper prepare a crystalline specimen of copper nitrate.

(*b*) From magnesium oxide prepare a crystalline specimen of magnesium sulphate.

(*c*) From lead carbonate prepare a crystalline specimen of lead nitrate.

(*d*) From lead nitrate solution prepare a crystalline specimen of lead chloride.

Lead chloride is insoluble in cold water but soluble in hot water.

In each case purify the specimens as completely as possible. In (*a*) (*b*) and (*c*) use excess of the copper, magnesium oxide, and lead carbonate respectively, in order to neutralise all the acid taken and so make a salt free from acid and easy to crystallise.

(5) From the given barium chloride $BaCl_2.2H_2O$ and potassium sulphate K_2SO_4, prepare specimens of barium sulphate and potassium chloride. Use the calculated quantities of the salts.

(6) From the given mixture, which contains equivalent quantities of sodium chloride and potassium nitrate, prepare specimens of these two salts.

(7) From potassium sulphate prepare a crystalline specimen of potassium hydrogen sulphate.

(8) Prepare a specimen of mercuric iodide, HgI_2, by rubbing together in a mortar the calculated quantities of mercury and iodine with a few drops of alcohol.

(9) From potassium sulphate and aluminium sulphate prepare crystals of ordinary alum.

CHAPTER XIV

ELEMENTARY VOLUMETRIC ANALYSIS

It has been found that acids and bases neutralise one another, forming salts and water. These reactions must take place between definite quantities of substances, just as do all other chemical reactions. If, then, the quantity of an acid in a solution is known, and the equation for its neutralisation by a base is known, it should be easy to find out the quantity of the base in the solution.

For the purposes of volumetric analysis it is convenient to fix a standard of strength for the solutions used. Only weak solutions are necessary. The standard solution chosen is what is called a *normal solution*.

A **normal solution** *of a substance is made by dissolving the*

gram equivalent weight of the substance in sufficient water to make a litre of solution.

By the gram equivalent weight of the substance is meant the amount of the substance which corresponds to 1 *gram of hydrogen.* Now, hydrochloric acid, HCl, contains 1 gram of hydrogen in 36.5 grams of acid, and gives off all this hydrogen when treated with zinc. Therefore 36.5 is the equivalent weight of hydrochloric acid.

$$\underset{}{Zn} + 2\underset{(73)}{HCl} = \underset{}{ZnCl_2} + \underset{(2)}{H_2}$$

Ninety-eight grams of sulphuric acid, the gram molecular weight of the acid, will give off, when treated with zinc, 2 grams of hydrogen. Therefore the equivalent weight of sulphuric acid is 49, that is, half its molecular weight.

$$\underset{}{Zn} + \underbrace{\underset{}{H_2SO_4}}_{2+32+4\times16=98} = \underset{}{ZnSO_4} + \underset{(2)}{H_2}$$

Again, one molecule of sodium hydroxide, NaOH, molecular weight 40, will neutralise one molecule of hydrochloric acid. Therefore 40, which is the molecular weight of caustic soda, is also the equivalent weight of caustic soda.

$$\underbrace{\underset{}{HCl}}_{1+35.5=36.5} + \underbrace{\underset{}{NaOH}}_{23+16+1=40} = \underset{}{NaCl} + \underset{}{H_2O}$$

One molecule of sodium carbonate, Na_2CO_3, molecular weight 106, will neutralise two molecules of hydrochloric acid, that is, 73 of hydrochloric acid. Therefore the equivalent weight of sodium carbonate is 53, *i.e.* half the molecular weight.

$$\underbrace{\underset{}{Na_2CO_3}}_{2\times23+12+3\times16=106} + \underbrace{\underset{}{2HCl}}_{2(1+35.5)=73} = \underset{}{2NaCl} + \underset{}{H_2O} + \underset{}{CO_2}$$

Decinormal solutions, one-tenth of the strength of normal solutions, are frequently used. The strength of a normal solution is often indicated by the letter N.

Thus $N.H_2SO_4$ is normal sulphuric acid solution, containing 49 grams of H_2SO_4 per litre of solution, that is, ·049 gram per c.c.

$\frac{N}{10}\cdot H_2SO_4$ is decinormal sulphuric acid containing 4.9 grams of sulphuric acid per litre of solution (.0049 per c.c.).

Any solution of which the strength is known, whether it is or is not a normal or decinormal solution, is called a **standard solution**.

When a solution of acid is run into a solution of an alkali, there must come a time when the addition of another drop of acid will more than neutralise the alkali not yet neutralised. To find out exactly when this takes place, substances called **indicators** are put into the solution. These indicators show by their colour when excess of acid or alkali is present. The indicators generally used are litmus solution, methyl orange solution, and phenol phthalein solution. The proper indicator must be selected for each neutralisation. Phenol phthalein, for example, cannot be used with weak bases like ammonia; nor can methyl orange be used with weak acids like oxalic acid. The effect of the presence of gases, such as carbon dioxide, on these indicators you will find out for yourself.

Only a very small quantity of methyl orange should be used, because the change of colour is very difficult to observe when the colour is deep.

For the purposes of volumetric analysis you will require a burette, a pipette, a measuring flask, ordinary flasks, and beakers.

A burette is a uniform glass tube, graduated from near the top downwards in tenths of a cubic centimetre. It is provided at the bottom with a glass stop-cock, or a rubber tube fitted with a jet and compressed by a pinch cork, or with an india-rubber tube fitted inside with a short piece of solid glass rod and at the end with a jet. The latter is shown in section at **AA** in Fig. 63.

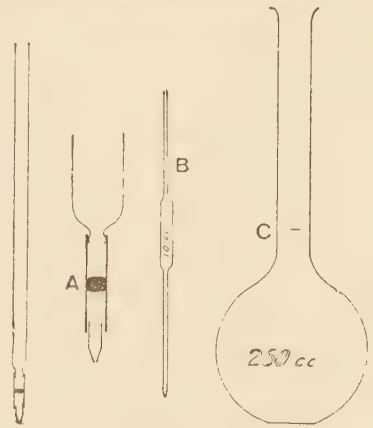


FIG. 63

The liquid is made to flow from the burette by pressing the

india-rubber to one side of the solid rod until a passage is made for the liquid. With a little practice one drop of liquid at a time can be let through.

A pipette, **B** in Fig. 63, is a tube with an elongated bulb in the middle. It is usually made to deliver 10 c.c., 20 c.c., or 25 c.c. of liquid. It is filled up to the mark by sucking with the mouth. The liquid is allowed to run out. The drop of liquid retained by the pipette should not be blown out. A measuring flask, **C**, Fig. 63, is made to hold a given volume of liquid, 100 c.c., 250 c.c., 1000 c.c., etc., when filled to the mark on the neck.

All these measuring vessels are meant for liquids at ordinary temperature, and therefore only cold liquids should be put into them.

When reading the burette, or filling the pipette or measuring flask, you will notice that the surface of the liquid is curved. This curved surface is called the *meniscus*. It is usual to take the bottom of the meniscus as the level of the liquid. When you read the burette, place a piece of white paper behind it and see that your eye, the bottom of the meniscus, and the mark on the burette are all in the same horizontal plane. Why?

Exp. 85—To test the accuracy of a burette, a 10 c.c. pipette, and a 100 c.c. measuring flask

Directions—Fill the burette with distilled water and run out some of the water in order to fill the jet. The bubble of air in the jet, when a burette like that in Fig. 63 is used, can easily be removed by turning the jet upwards and driving out the air with water from the burette. Adjust the level of the liquid in the burette to 0 c.c.

Weigh a small dry flask. Run into the flask 5 c.c. of water at a time, and weigh each portion. If the burette is accurate the water from any 5 c.c. will weigh exactly the same as the water from any other 5 c.c. of the burette. 1 c.c. of pure water weighs 1 gram.

Next fill your pipette with distilled water and weigh the water in the same way.

Test the measuring flask, (*a*) by weighing it empty and full of distilled water, and (*b*) by means of your burette and pipette.

Exp. 86—To observe the effect of acids, alkalis, and carbon dioxide on indicators

Directions—

(1) Take purple litmus solution. To a little litmus add a few drops of acid, and then add alkali solution until the colour changes.

(2) Pass carbon dioxide through cold dilute litmus solution and then boil. Note the colour changes. Could litmus be used if a solution of sodium carbonate were being neutralised or *titrated*, as the term is, with acid?

Repeat these tests with methyl orange and phenol phthalein and state in each case the effect of the carbon dioxide. Which indicator would be the best for the sodium carbonate titration?

Exp. 87—Given a standard solution of hydrochloric acid, to find the strength of a solution of caustic soda

$$\underset{23+16+1}{NaOH} + \underset{1+35.5}{HCl} = NaCl + H_2O$$
$$=40 \qquad =36.5$$

Directions—Wash out your burette with a few c.c. of hydrochloric acid solution and throw away the washings. Fill the burette with the acid solution and fix it vertically on its stand.

Measure out with a pipette 10 c.c. of caustic soda solution. Put the solution into a small conical flask. Next add to the soda solution any indicator you think suitable. Place the flask on a piece of white paper or on a white tile, and see that the jet of the burette is just inside the mouth of the flask.

Now run in acid solution, one c.c. at a time. After each addition gently twirl round the flask to thoroughly mix the liquids. Repeat until the indicator changes colour. Read the burette and write down the reading. You have made a rough titration, which tells you, correct to one c.c., the amount of liquid required to neutralise 10 c.c. of alkali. Let the reading of the burette be 12.0 c.c.

Next wash out the flask. Again put in 10 c.c. of soda and a few drops of indicator. Run in from the burette a volume of acid less by one c.c. than that used in the first titration. Then add acid one drop at a time, shaking after each addition,

until the indicator changes colour. You will now have found the volume of acid required to an accuracy of one drop.

Do two more titrations and take the mean of the 2nd, 3rd, and 4th titrations. The first titration was not accurate.

Suppose that the mean of three titrations is 11.3 c.c. and the strength of the acid provided is .00342 gram per c.c.

From the equation it is evident that

36.5 grams of hydrochloric acid neutralise 40 grams of caustic soda.

$\therefore$ 1 gram ,, ,, ,, neutralises $\frac{40}{36.5}$,, ,, ,, ,,

The amount of acid used in the titration is 11.3 c.c.

$\therefore$ $11.3 \times .00342$ grams of hydrochloric acid neutralise

$$\frac{40}{36.5} \times \frac{11.3 \times .00342}{1} \text{ grams of caustic soda.}$$

But this weight of caustic soda was contained in 10 c.c. of the solution.

$\therefore$ 1 c.c. of caustic soda solution contains $\frac{40}{36.5} + \frac{11.3 \times .00342}{10}$ grams of caustic soda.

$= .00424$ **gram of NaOH.**

Exp. 88—Given a standard solution of hydrochloric acid, to find the strength of a solution of sodium carbonate

$$\underset{2\times23+12+3\times16}{Na_2CO_3} + \underset{2(1+35.5)}{2HCl} = 2NaCl + CO_2 + H_2O$$
$$= 106 \qquad = 73$$

Directions—Proceed in the same way as in the last experiment. Do 4 titrations.

Be certain that you choose the proper indicator, for carbon dioxide will be present.

If the quantity of acid required for the first titration is much less than 10 c.c., a larger quantity of sodium carbonate should be taken for the others in order to reduce the error of the experiment. For suppose that 3 c.c. of acid neutralise 10 c.c. of soda. An error of .1 c.c. in the titration makes an error of 1 in 30, or 3.3 per cent. in the result. If 40 c.c. of Na_2CO_3 are used, 12 c.c. of acid are required. An error of .1 c.c. now gives an error of only 1 in 120, or .83 per cent. in the result.

The acid should always be put into the burette, because the change of colour of the indicator, if always in the same direction, can be noted with greater accuracy than if it is sometimes in one direction and sometimes in another.

Exp. 89—Given a standard solution of sodium carbonate, to find the strength of a solution of sulphuric acid

$$\underbrace{Na_2CO_3}_{106} + \underbrace{H_2SO_4}_{98} = Na_2SO_4 + H_2O + CO_2$$

Directions—Carbon dioxide will be present, and therefore the indicator must be carefully chosen. Put the acid in the burette and do at least four titrations.

Exp. 90—To prepare a normal solution of oxalic acid

Directions— Hydrated oxalic acid has the formula $H_2C_2O_4.2H_2O$. Both hydrogen atoms in the $H_2C_2O_4$ are replaceable by metals. Calculate the equivalent weight of the anhydrous acid and also of the hydrated acid. Next calculate the weight of hydrated oxalic acid required to make 250 c.c. of a normal solution of oxalic acid.

Accurately weigh out the calculated quantity, dissolve the weighed acid in distilled water, put the solution into a 250 c.c. measuring flask, make up to the mark with distilled water, and thoroughly mix.

Exp. 91—To make a normal solution of sodium carbonate

Directions—Calculate the weight of sodium carbonate, Na_2CO_3, necessary to make up 250 c.c. of a normal solution.

Heat about 25 grams of pure bicarbonate of soda in a porcelain dish to dull redness over a bunsen flame for about thirty minutes. This converts the bicarbonate to carbonate.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$
Bicarbonate

Heat until the weight of the dish is constant.

Allow to cool. Weigh out accurately the calculated quantity of sodium carbonate, dissolve in water, and make up to 250 c.c.

Exp. 92—To determine whether the above normal solutions of oxalic acid and sodium carbonate have been accurately made

$$Na_2CO_3 + H_2C_2O_4 = Na_2C_2O_4 + H_2O + CO_2$$

Directions—If the solutions have been accurately made,

1 c.c. of sodium carbonate should require 1 c.c. of oxalic acid to neutralise it.

The chief difficulty of this titration is in the selection of the indicator.

Methyl orange will not do, because it is not sufficiently delicate to give a sharply marked *end-point* with weak acids, such as oxalic acid. Phenol phthalein cannot be used with carbon dioxide present. There remains only litmus. Litmus can be used with weak acids, but it is affected by carbon dioxide. If, however, the solution is boiled after each addition of oxalic acid, the carbon dioxide is expelled, and a sharp end-point is obtained.

Take 10 c.c. of sodium carbonate solution, dilute with about 20 c.c. of water, add litmus, run in acid until the litmus begins to change colour, and boil until the litmus becomes blue again. Add acid, drop by drop, boiling after each addition, until finally, boiling will not cause the litmus to become blue again. The sodium carbonate is now completely converted into sodium oxalate. Repeat the titration.

Exp. 93—To prepare a normal solution of sulphuric acid

Directions—Calculate the quantity of strong sulphuric acid required to make 250 c.c. of a normal solution.

Roughly weigh into a beaker an amount of sulphuric acid greater by 2 or 3 grams than the amount calculated. Dilute with water, cool if necessary, transfer to a 250 c.c. measuring flask, and make up to 250 c.c. with distilled water.

Find the strength of the sulphuric acid by titration with normal sodium carbonate solution. Next calculate the volume of water which it will be necessary to add to 100 c.c. of the sulphuric acid to make it of normal strength.

Calculation—Suppose that the strength of the sulphuric acid is found to be .061 gram per c.c.

Let x be the number of c.c. of water to be added to 100 c.c. of the sulphuric acid to make it normal.

Normal sulphuric acid has the strength .049 gram per c.c. The weight of H_2SO_4 in 100 c.c. of your solution is $100 \times .061$ grams. The volume of the sulphuric acid after dilution with x c.c. of water will be $100+x$ c.c.

$\therefore$ $100+x$ c.c. contain $(100+x) \times .049$ grams of H_2SO_4.

The amount of sulphuric acid is not altered by dilution.

$$\therefore 100 \times .061 = (100 + x) \times .049$$
$$\therefore .049\,x = 6.1 - 4.9$$
$$\therefore x = \frac{1.2}{.049} = \mathbf{24.5\ c.c.\ of\ water.}$$

Measure out the 100 c.c. of sulphuric acid, add to it from a burette the calculated volume of water, and find out by titration whether 10 c.c. of the normal sulphuric acid exactly neutralises 10 c.c. of the normal sodium carbonate solution.

Exp. 94 – To prepare a normal solution of caustic soda

Directions—Calculate the weight of caustic soda necessary to make about 250 c.c. of normal solution. Weigh out quickly 2 or 3 grams more than this amount of solid caustic soda. Dissolve in water, and make up to 250 c.c.

Find the strength of this solution by means of your normal sulphuric acid or normal oxalic acid. Calculate, and add from a burette, the water necessary to make up 100 c.c. of the solution to normal strength. Check the strength of the normal solution by titration.

Exp. 95—To find the strength of a solution of barium chloride

$$BaCl_2 + Na_2CO_3 = \underset{\text{(insoluble)}}{BaCO_3} + 2NaCl$$

Directions—Take 50 c.c. of the given solution, and add to it more than enough standard sodium carbonate solution, say 200 c.c., to completely precipitate all the barium as carbonate. The volume of the sodium carbonate solution must be known.

Mix thoroughly, filter from the barium carbonate, and titrate part of the filtrate, containing the unused sodium carbonate, with standard acid.

Calculation—Suppose that the strength of the original sodium carbonate solution added was .053 gram per c.c., and that after precipitation and filtration the strength of the sodium carbonate solution was found to be .022 gram per c.c.

The total weight of sodium carbonate added was $200 \times .053$ grams. The bulk of the liquid, after addition of sodium carbonate, was 250 c.c.

$\therefore$ The total weight of the unused sodium carbonate was $250 \times .022$ grams.

∴ The weight of sodium carbonate reacting with barium chloride was $200 \times .053 - 250 \times .022 = 5.1$ grams.

The equation shows that—

106 grams of sodium carbonate react with 208 grams of barium chloride.

∴ 1 gram of sodium carbonate reacts with $\frac{208}{106}$ grams of barium chloride.

∴ 5.1 grams of sodium carbonate react with $\frac{208}{106} \times 5.1$ grams of barium chloride.

But this weight of barium chloride was contained in 50 c.c.

∴ 1 c.c. of barium chloride solution contained $\frac{208}{106} \times \frac{5.1}{50}$

= .200 gram of barium chloride.

Exp. 96—To find the strength of a solution of copper sulphate

Directions—Proceed exactly as in the last experiment, but use standard sodium hydrate solution instead of sodium carbonate.

$$\underset{63+32+64}{\underset{=159}{CuSO_4}} + \underset{2(23+16+1)}{\underset{=80}{2NaOH}} = Na_2SO_4 + Cu(OH)_2$$

Exp. 97—To find the equivalent weight of magnesium

Directions—Weigh out about .3 or .4 gram of clean magnesium ribbon and dissolve it in 100 c.c. (accurately measured) of normal sulphuric acid.

Fill a burette with N. caustic soda and titrate the acid left.

Calculate the weight of acid which has reacted with the magnesium, and then calculate the weight of magnesium which will react with the equivalent weight of sulphuric acid.

This weight will be the equivalent weight of magnesium.

Exp. 98—To find the equivalent of aluminium

Directions—Use 50 c.c. of ordinary dilute hydrochloric acid (1 to 4 of water), and .3 to .4 gram of thin aluminium sheet or powder. Warm gently. Find the strength of the hydrochloric acid used by diluting 50 c.c. to 250 c.c., and titrating with normal sodium hydrate. Next titrate the acid in which the aluminium has been dissolved. Calculate the weight of the metal which reacts with the equivalent weight of the acid.

Exp. 99—To find the equivalent weight of zinc

Directions—Use dilute bench hydrochloric acid or sulphuric acid. Use about .5 gram of thin zinc foil.

Exp. 100—To find the equivalent of an insoluble base such as zinc oxide or copper oxide

Directions—Weigh out accurately 1 to 2 grams of the base, and dissolve it in 100 c.c. of normal acid, choosing an acid which readily dissolves the base, *e.g.* hydrochloric acid for zinc oxide.

Calculate the equivalent weight of the base, *i.e.* the weight of the base which corresponds to the equivalent weight of the acid.

Exp. 101—To find the weight of metallic iron in 1 c.c. of a ferrous sulphate solution by titration with decinormal potassium permanganate

$$10FeSO_4 + 2KMnO_4 + 9H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + 2KHSO_4 + 8H_2O$$

10×56 $2(39+55+4\times16)$

$=560$ $=316$

Directions—Put the permanganate in the burette. Take 10 c.c. of cold ferrous sulphate solution and add to it about 20 c.c. of dilute sulphuric acid (1 to 4 of water). Run in permanganate from the burette until a permanent pink colouration is obtained. All the iron has then been oxidised.

Calculation—Two molecules of permanganate contain 5 atoms of oxygen available for oxidising purposes. Five atoms of oxygen will oxidise 10 atoms of hydrogen. Therefore the equivalent of potassium permanganate for oxidising purposes is $\frac{316}{10}=31.6$.

$\therefore \frac{N}{10}\cdot KMnO_4$ contains .00316 gram of $KMnO_4$ per c.c. The strength of a ferrous sulphate solution is generally expressed as weight of metallic iron per c.c.

Exp. 102—To find the weight of iron in 1 c.c. of a ferric sulphate solution

Directions—The ferric sulphate must first be reduced to ferrous sulphate. This may be done in one or two ways.

(*a*) By means of zinc dust. Put 50 c.c. of the ferric sulphate solution into a beaker, add about one-tenth of a test-tubeful

of zinc dust, and then 10 c.c. of dilute sulphuric acid. Shake well, wait a minute or two, and shake again. Into the liquid put a dry reversed filter,* draw off 10 c.c. of the clear liquid from the filter and titrate it with permanganate solution. In your calculation do not neglect the volume of sulphuric acid added.

(*b*) By means of granulated zinc. Into a flask put 100 c.c. of the ferric sulphate solution, add a few pieces of granulated zinc, and then about 100 c.c. of dilute sulphuric acid. Fit the flask with a cork carrying a tube about 20 inches long, on the end of which is fitted a bunsen valve (see page 214). Gently warm the contents of the flask until the zinc has all dissolved. Cool the flask. When it is cold, quickly transfer the contents to a 250 c.c. measuring flask, and make up the volume to 250 c.c. with distilled water. Mix thoroughly and titrate the solution with standard permanganate solution.

Exp. 103—To find the strength of a solution of potassium permanganate by means of standard oxalic acid solution

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

$5(2+24+64)$ 316

$=450$

Directions—Take 10 c.c. of oxalic acid, dilute with about 30 c.c. of water, add 20 c.c. of dilute sulphuric acid, and warm the mixture to 60° C., a temperature that can just be borne by the hand. Run in permanganate solution until a permanent pink is obtained.

PRACTICAL EXERCISES

(1) Find the strength of a bench ammonium hydrate.

(2) Find the percentage of sulphuric acid in commercial strong sulphuric acid.

(3) Find the strength of the bench dilute nitric acid.

(4) Find the percentage of Na_2CO_3 in a given sample of washing soda.

(5) Find the strength of a solution of acetic acid.

$$C_2H_4O_2 + NaOH = C_2H_3O_2Na + H_2O$$

(6) Find the strength of a solution of calcium chloride.

(7) From metallic iron make a decinormal solution of ferrous sulphate.

(8) Find the strength of a solution of ammonium chloride. Ammonium salts boiled with excess of caustic soda for some minutes lose all their ammonia. Thus—

$$NH_4Cl + NaOH = NaCl + H_2O + NH_3$$

* A reversed filter consists of a glass tube about 10 cm. long and 2 cm. wide, across the bottom of which is tied a filter paper.

(9) The given solution contains ferrous sulphate and ferric sulphate. Find the weight of metallic iron in 1 c.c.

(10) Find the weight of ammonium oxalate, $(NH_4)_2C_2O_4$, in 1 c.c. of the given solution.

CHAPTER XV

CHLORINE AND HYDROCHLORIC ACID

Exp. 104—To prepare chlorine and investigate its properties

Directions—Prepare chlorine by warming with strong hydrochloric acid manganese dioxide, moistened with water. Wash the gas free from hydrochloric acid gas by means of water, and collect by downward displacement of air. The operation should be carried out in a draught chamber.

Test for the properties as usual.

Also try the following experiments :—

(1) Into a jar of the gas throw some finely powdered antimony. Into the same jar a piece of Dutch metal might afterwards be introduced.

(2) Into a jar of the gas introduce a filter paper moistened with turpentine, and take note of the products, both solid and gaseous.

(3) Into a jar of the gas introduce a jet of burning hydrogen. When the jet has gone out, smell the residual gas. Can you name it ?

(4) Make a solution of chlorine in about 100 c.c. of water. Try the effect of the solution on (*a*) petals of flowers, (*b*) paper smeared with writing ink, (*c*) printed paper, (*d*) turkey red twill, (*e*) potassium bromide solution, and (*f*) potassium iodide solution. If you have enough solution left, fill a long tube with it, invert the tube in a porcelain dish containing water, and allow it to stand in direct sunlight until the colour of the chlorine has disappeared. Then carefully turn up the tube on your thumb and test the gas which has collected with a glowing splint. Test the liquid with litmus solution.

Exp. 105—To prepare hydrochloric acid and investigate its properties

Directions—Prepare the gas by heating sodium chloride

with sulphuric acid, diluted with its own volume of water. Collect by downward displacement of air.

Determine the properties of the gas in the usual way.

Make a solution of the gas by passing it into water and try the effect of the solution on carbonates, metals, and silver nitrate solution. Try to expel the gas from a small quantity of the solution by boiling, and test the solution left with (1) sodium carbonate and (2) silver nitrate. Is the gas expelled from solution on boiling?

Exp. 106—To show the presence of hydrogen in hydrochloric acid gas

Directions—Pass hydrochloric acid, dried by strong sulphuric acid, over iron filings heated in a hard glass tube which is fitted with a jet. Collect the issuing gas over water, and test it for hydrogen.

Exp. 107—To show the presence of chlorine in gaseous hydrochloric acid

Directions—Pass hydrochloric acid over manganese dioxide, heated in a hard glass tube. Test the issuing gas for chlorine by wet litmus paper and starch iodide paper. Also smell the gas and note its colour.

Exp. 108—To prepare specimens of chlorides of the metals

Directions—Prepare specimens of metallic chlorides from (1) a metal; (2) the oxide of a metal; (3) the hydroxide of a metal; (4) the carbonate of a metal; (5) a solution of a soluble salt of lead, mercury, or silver. Lead, mercurous and silver chlorides are insoluble.

In each case prove by testing with (*a*) strong sulphuric acid, (*b*) strong sulphuric acid and manganese dioxide, (*c*) a solution of silver nitrate, that the specimen you have obtained is a chloride. Use the solid chloride in (*a*) and (*b*), and a solution of the chloride in (*c*).

CHLORINE. Symbol, Cl

History—Chlorine was discovered in 1774 by Scheele, who obtained it by heating ores of manganese with strong hydrochloric acid. Up to the time of Davy it was believed to be a compound of oxygen and hydrochloric acid. Davy, however, showed that it contained no oxygen, and that it

could not be split up into a simpler substance by any known means, *i.e.* that chlorine was an element. He named it chlorine on account of its greenish-yellow colour (Gk. χλωρός).

Occurrence—Chlorine never occurs uncombined in nature. Its most common compound is common salt, NaCl, which occurs in large quantities in the sea and in rock salt deposits in many parts of the world. Magnesium chloride and potassium chloride are found in sea water, and considerable deposits of these substances occur in the Stassfurt deposits in Saxony.

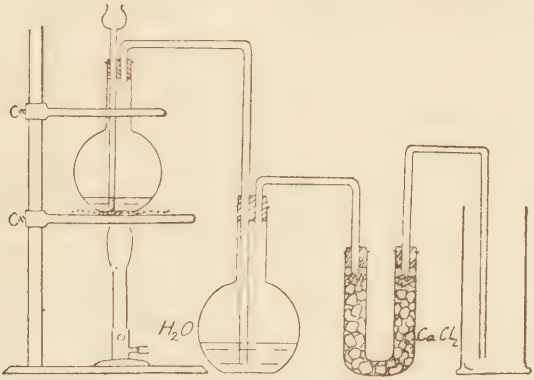


FIG. 64

Formation—(1) Chlorine is most readily prepared in the laboratory from manganese dioxide and strong hydrochloric acid, Fig. 64. The gas may be dried, if necessary, by means of a calcium chloride tube. The water in the wash-bottle frees the gas from hydrochloric acid gas.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$

(2) Instead of hydrochloric acid, sodium chloride and strong sulphuric acid, the materials from which this substance is prepared, may be used. A mixture of 1 part of common salt, 1 part of manganese dioxide, and 4 parts of strong sulphuric acid, diluted with its own volume of water, reacts on warming, according to the equation (Klason)—

$$4NaCl + MnO_2 + 3H_2SO_4 = 2NaHSO_4 + Na_2SO_4 + MnCl_2 + 2H_2O + Cl_2$$

The equation—

$$2NaCl + MnO_2 + 3H_2SO_4 = 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2$$

which is sometimes employed, is not quite correct, as some chlorine remains in combination with manganese.

(3) Chlorine can also be obtained by heating oxidising agents with strong hydrochloric acid.

Thus—

$$\underset{\text{Red lead}}{Pb_3O_4} + 8HCl = \underset{\text{Lead chloride}}{3PbCl_2} + 4H_2O + Cl_2$$

$$\underset{\substack{\text{Potassium}\\\text{bichromate}}}{K_2Cr_2O_7} + 14HCl = 2KCl + \underset{\substack{\text{Chromium}\\\text{chloride}}}{2CrCl_3} + 7H_2O + 3Cl_2$$

$$\underset{\substack{\text{Potassium}\\\text{chlorate}}}{4KClO_3} + 12HCl = \underset{\substack{\text{Potassium}\\\text{chloride}}}{4KCl} + 6H_2O + \underset{\substack{\text{Chlorine}\\\text{peroxide}}}{3ClO_2} + 9Cl$$

The mixture of chlorine and chlorine peroxide obtained from potassium chlorate was discovered by Davy, who named it "euchlorine."

(4) Chlorine is manufactured in large quantities for the purpose of making bleaching powder.

One process, *Deacon's process*, consists in passing a mixture of air and hydrochloric acid over pumice, impregnated with cupric chloride and heated to 400° C. At this temperature the cupric chloride splits up into cuprous chloride and chlorine. Thus, $2CuCl_2 = Cu_2Cl_2 + Cl_2$.

The cuprous chloride has a chemical attraction for chlorine, and this attraction, together with the attraction of the oxygen of the air for the hydrogen of the hydrochloric acid, seems to be sufficient to overcome the mutual attraction of the hydrogen and chlorine in hydrochloric acid.

The final result may be expressed—

$$O + 2HCl = H_2O + Cl_2$$
$$(+Cu_2Cl_2) \quad (+Cu_2Cl_2)$$

Chlorine, mixed with much nitrogen from the air, is thus obtained. It is used for making bleaching powder.

Another process, *Weldon's process*, gives a much purer chlorine. Manganese dioxide is heated in stone stills with strong hydrochloric acid. If the manganese was wasted, the process would not pay. The manganese chloride solution is treated with chalk to neutralise the free acid and to precipitate iron as hydroxide. The solution is then mixed with slaked lime, warmed with steam, and oxidised by blowing air through

it. By this means *Weldon's mud*, a mixture of compounds of lime with manganese dioxide, is obtained. This mud can be used for the preparation of more chlorine from hydrochloric acid.

Much commercial chlorine is now obtained by the electrolysis of a solution of sodium chloride in a Hargreaves-Bird cell. See page 347. The chlorine obtained is very pure. The chlorine is dried and sent into the market in the liquid state in steel cylinders. Moist liquid chlorine attacks steel.

Properties—Atomic weight = 35.5. Density = 35.5. Molecular weight = 71.

Chlorine is a greenish-yellow gas with a very strong irritating smell. It attacks the membranes lining the nose and throat, and produces all the symptoms of a severe cold. Inhaled in the pure state it causes death.

It is about two and a half times as heavy as air.

Water, at ordinary temperatures, dissolves three times its volume of chlorine. The solution, cooled to 0° C., deposits yellow crystals of chlorine hydrate, $Cl_2.10H_2O$. It was by heating these crystals in a strong closed bent tube, Fig. 65, one limb of which was cooled in a freezing mixture, that Faraday first obtained liquid chlorine. The liquid is pale yellow, boils at −33.6° C., and freezes at −102° C. to a yellow crystalline solid.

FIG. 65

Gaseous chlorine is very active chemically. A taper burns in it with a smoky flame ; phosphorus ignites spontaneously in the gas, giving phosphorus chloride, PCl_3, and phosphorus pentachloride, PCl_5. Some metals, in a finely divided state or in the form of thin leaf, light spontaneously in the gas. Thus, powdered antimony and Dutch metal (thin copper foil) take fire spontaneously in chlorine, giving chlorides. Sodium potassium, and magnesium, if lighted and plunged into the gas, continue to burn brightly, forming sodium chloride NaCl, potassium chloride KCl, and magnesium chloride $MgCl_2$. If a current of chlorine is passed over mercury which is treated in a hard glass tube, a flame is seen over the

mercury and a white deposit of mercuric chloride, $HgCl_2$, is formed on the cool part of the tube.

Chlorine has a great chemical attraction for hydrogen. A jet of hydrogen burns in chlorine, giving hydrochloric acid. Equal volumes of hydrogen and chlorine, mixed and exposed to direct sunlight or to a flame, explode violently, giving hydrochloric acid gas.

$$H_2 + Cl_2 = 2HCl$$

Chlorine will take out hydrogen from many compounds of hydrogen and carbon. Thus turpentine, $C_{10}H_{16}$, when poured on a filter paper and introduced into the gas, is instantly inflamed, owing to the combination of hydrogen with chlorine. The inside of the jar is blackened by the carbon liberated.

Chlorine under the influence of direct sunlight decomposes water. If a large jar of chlorine water is exposed to sunlight, the colour of the chlorine gradually disappears, oxygen is set free, and a solution of hydrochloric acid is formed.

$$H_2O + Cl_2 = 2HCl + O$$

The bleaching power of chlorine also depends on its attraction for hydrogen. Chlorine will not bleach unless water is present. Thus, if a piece of turkey red cloth be thoroughly dried in an air bath, and then put into a jar of chlorine which has been well dried by means of calcium chloride, the cloth is only very slowly bleached. If no trace of water is present, the cloth is not bleached at all. It would seem, therefore, that water aids the bleaching action of chlorine. It is supposed that the water reacts with chlorine, giving hypochlorous acid and hydrochloric acid.

Thus, $H_2O + Cl_2 = HCl + HClO$

The hypochlorous acid gives up its oxygen atom to the dye oxidising it to colourless substances. In some cases the dye combines directly with the chlorine, colourless substances being produced.

Chlorine bleaches only vegetable colouring matter. Writing ink usually consists of a compound of iron with tannic and gallic acids, vegetable acids. It is readily bleached by chlorine. Printers' ink is usually made from lamp black (carbon), and is not affected by the gas.

Chlorine displaces bromine and iodine from solutions of bromides and iodides.

$$2KBr + Cl_2 = 2KCl + Br_2$$
$$2KI + Cl_2 = 2KCl + I_2$$

The bromine is easily recognised by its red colour and smell, and the iodine by the blue colour it gives with starch solution.

HYDROCHLORIC ACID (*Hydrogen chloride*), HCl

History—In solution in water this acid was known to the alchemists. Its solution mixed with nitric acid forms *aqua regia*, a liquid much valued by the old chemists on account of its great solvent power. Aqua regia dissolves the "king of metals," as gold was called.

In 1648 Glauber obtained the solution by heating common salt with strong sulphuric acid. Priestley, however, first collected and examined the gas. He collected it over mercury.

Occurrence—It occurs in the gaseous state in volcanic gases, and in solution in the gastric juices of animals.

Formation—(1) Hydrochloric acid is prepared by heating common salt with sulphuric acid, diluted with its own volume of water. To purify the gas from water and mechanically carried particles of sulphuric acid, it is passed through a wash-bottle containing pumice covered with strong sulphuric acid.

$$NaCl + H_2SO_4 = \underset{\text{Acid sodium sulphate}}{NaHSO_4} + HCl$$

When sulphuric acid, diluted with water, is used for the preparation, the action does not proceed beyond this stage. If strong sulphuric acid and excess of the salt are used, both atoms of hydrogen are displaced from the acid.

$$2NaCl + H_2SO_4 = \underset{\text{Normal sodium sulphate}}{Na_2SO_4} + 2HCl$$

Many other metallic chlorides might be used instead of sodium chloride. Thus—

$$2KCl + H_2SO_4 = K_2SO_4 + 2HCl$$
$$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl$$
$$CuCl_2 + H_2SO_4 = CuSO_4 + 2HCl$$

(2) The acid may be obtained by direct combination of equal volumes of hydrogen and chlorine.

$$H_2 + Cl_2 = 2HCl$$

This combination takes place slowly in diffused daylight, but with a violent explosion in direct sunlight.

The combination of the gases may be shown by filling, in a dim light, a stout glass tube with a stop-cock at each end, and with two platinum wires sealed into its sides, with a mixture of equal volumes of chlorine and hydrogen, obtained by electrolysis of strong hydrochloric acid. See Fig. 66.

The gases are made to combine by passing an electric spark. When one end of the tube is opened under mercury, no mercury is drawn into the tube. Therefore the tube is still full of gas. When one end of the tube is opened under water, the water completely fills the tube, and the solution

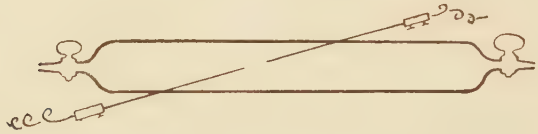


FIG. 66

formed has all the properties of a weak solution of hydrochloric acid. The experiment may be made more complete by filling a second tube, closed at one end, with the same mixture of gases and inverting the tube in caustic potash solution. The chlorine, occupying exactly half the tube, is absorbed and an equal volume of hydrogen is left. That the gas left is hydrogen is shown by burning it.

Properties—Density = 18.25. Molecular weight = 36.5. Solubility = 500 volumes in one volume of water at 0° C.

Hydrochloric acid is a colourless gas, with an irritating smell and a sour taste. It is about $1\frac{1}{3}$ times as heavy as air. It is very soluble in water.

Its great solubility may be illustrated by means of the apparatus shown in Fig. 67. This consists of a round-bottomed flask, fitted with an india-rubber cork carrying a glass tube drawn out to a jet. The flask is filled with hydrochloric acid gas and the end of the glass tube is placed in water coloured with blue litmus. By gently warming the flask and allowing it to cool, a few drops of water can be drawn

into it. A partial vacuum is formed by the rapid solution of the gas in these drops of water and the water in the vessel is driven—by the pressure of the air on it—with great force, in a fountain-like jet, into the flask. The dissolved acid changes the colour of the water from blue to red.

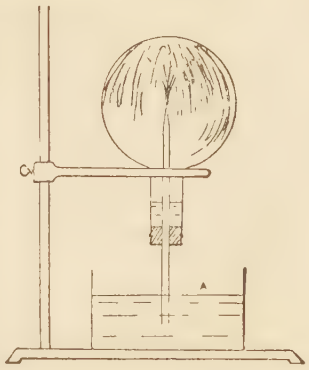


FIG. 67

In consequence of its attraction for water, hydrochloric acid fumes in moist air. The fumes consist of minute globules of a solution of the gas.

The solution of the gas, if weak, on boiling becomes stronger by loss of water, and if strong, becomes weaker by loss of hydrochloric acid, until a solution containing about 20 per cent. of hydrochloric acid, and boiling at 110° C., is obtained. This solution does not, however, contain a definite compound of the gas and water, because the percentage of hydrochloric acid present depends on the pressure under which the solution is boiled.

The strongest solution of the gas in water at ordinary temperature has a specific gravity of 1.2 and contains about 42 per cent. of HCl. The pale yellow colour of commercial hydrochloric acid is due to the presence of impurities, of which ferric chloride is the most important.

Hydrochloric acid solution reacts with carbonates, giving carbon dioxide and a chloride, and with many metals, giving hydrogen and a chloride of the metal.

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$$

$$Zn + 2HCl = ZnCl_2 + H_2$$

Zinc chloride

$$Fe + 2HCl = FeCl_2 + H_2$$

Ferrous chloride

$$Mg + 2HCl = MgCl_2 + H_2$$

Magnesium chloride

$$Sn + 2HCl = SnCl_2 + H_2$$

Stannous chloride

It has hardly any reaction with copper or mercury.

Like all acids, it neutralises bases and alkalis, giving salts and water.

$$NaOH + HCl = NaCl + H_2O$$
$$MgO + 2HCl = MgCl_2 + H_2O$$

Gaseous hydrochloric acid will not burn and will not support the combustion of a taper, sulphur, or phosphorus. Sodium will readily burn in it, forming sodium chloride and hydrogen.

Composition of hydrochloric acid

The presence of chlorine in the gas has been proved by passing it over heated manganese dioxide.

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

The presence of hydrogen has been proved by passing the gas over heated iron filings.

$$Fe + 2HCl = FeCl_2 + H_2$$

These experiments do not, however, prove that hydrogen and chlorine are the only elements present.

In the second method of formation, however, experiments were described which clearly show that the acid contains nothing but hydrogen and chlorine. The experiments show that one volume of hydrogen combines with one volume of chlorine to give two volumes of hydrochloric acid. That two volumes of hydrochloric acid were produced, was shown by opening the tube, after the explosion, under mercury. The tube must have been completely full of hydrochloric acid, because no mercury was drawn up. This is in accordance with Gay Lussac's Law (*q.v.*).

Now, equal volumes of chlorine, hydrogen, and hydrochloric acid contain equal numbers of molecules (Avogadro's Law).

$\therefore$ n molecules of chlorine combine with n molecules of hydrogen to form $2n$ molecules of hydrochloric acid.

But each molecule of hydrogen contains 2 atoms and each molecule of chlorine contains 2 atoms.

$\therefore$ $2n$ atoms of chlorine combine with $2n$ atoms of hydrogen to give $2n$ molecules of hydrochloric acid.

$\therefore$ 1 atom of chlorine combines with 1 atom of hydrogen to give 1 molecule of hydrochloric acid, *i.e.* the molecule of

hydrochloric acid contains 1 atom of chlorine and 1 atom of hydrogen.

∴ The formula of hydrochloric acid is HCl.

Electrolysis of hydrochloric acid solution

Fig. 68 shows an apparatus which may be used for the electrolysis of hydrochloric acid.

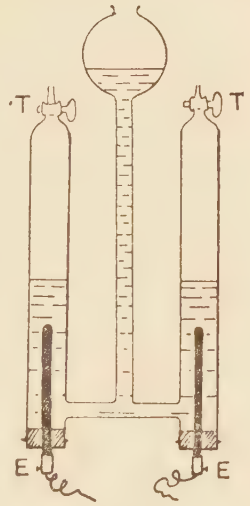


FIG. 68

Carbon electrodes, **EE**, are used, because chlorine attacks metals. The apparatus is filled with strong hydrochloric acid into which chlorine has been passed for some time, and an electric current is passed for half an hour with the taps **TT** open. This must be done in order to saturate completely the hydrochloric acid with chlorine. Why must the hydrochloric acid be saturated ? The taps are then closed, and the current is passed for some minutes. Chlorine comes off at the anode and hydrogen at the kathode. The volumes of hydrogen and chlorine evolved are equal. The hydrogen does not come from the water, because the same weight of water is present after the experiment as before it. The weight of hydrochloric does decrease, and it can be proved that this weight is equal to the weight of the chlorine and hydrogen produced. The experiment therefore shows that hydrochloric acid consists of a combination of equal volumes of chlorine and hydrogen.

FIG. 69

$$2HCl = H_2 + Cl_2$$

Analysis of hydrochloric acid by means of sodium amalgam

A U tube with stop-cocks at A and

B is filled with dry mercury. See Fig. 69. The limb **AC** is then half filled with dry hydrochloric acid gas, and mercury is drawn out from **B** until the mercury is at the same level in both limbs. An india-rubber ring is then put on **AC** at the level of the mercury. A solution of sodium in mercury, *i.e.* liquid sodium amalgam, is poured into the limb **BD** until it is completely filled. The thumb is then tightly pressed on the open end **D** of the tube and the gas passed several times through the sodium amalgam. The gas is finally passed back into **AC** and the thumb removed. The mercury is then adjusted until it is level in both limbs. The volume of gas is noted. The volume is found to be half the original volume of the hydrochloric acid. The gas on testing is found to be hydrogen.

$$2HCl + 2Na = 2NaCl + H_2$$

Calculation—Hydrochloric acid contains only chlorine and hydrogen.
The chlorine combines with sodium, and hydrogen is set free.
2 volumes of hydrochloric acid contain 1 volume of hydrogen.
∴ 2 molecules of hydrochloric acid contain 1 molecule of hydrogen (Avogadro's Law).
∴ 2 molecules of hydrochloric acid contain 2 atoms of hydrogen.
∴ 1 molecule ,, ,, contains 1 atom ,,
∴ The formula of hydrochloric acid is HCl, HCl_2, or HCl_x.
The density of hydrochloric acid is 18.25.
∴ The molecular weight of hydrochloric acid is 36.5.
∴ A molecule of hydrochloric acid contains $36.5 - 1 = 35.5$ parts by weight of chlorine.
35.5 is the weight of one atom of chlorine.
∴ 1 molecule of hydrochloric acid contains 1 atom of hydrogen and 1 atom of chlorine.
∴ The formula of hydrochloric acid is HCl.

Chlorides

Chlorides are compounds of elements with chlorine.

(A) Metallic chlorides are readily made by—

(1) Action of metal and chlorine.

$$2Na + Cl_2 = 2NaCl$$

(2) Solution of the metal, metallic oxide, hydroxide, or carbonate in hydrochloric acid, and evaporation to dryness or to the crystallising point.

$$Zn + 2HCl = ZnCl_2 + H_2$$
$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$$
$$Cu(OH)_2 + 2HCl = CuCl_2 + 2H_2O$$
$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

(3) Precipitation of a solution of a suitable salt of the metal with a soluble chloride.

$$Pb(NO_3)_2 + 2HCl = \underset{\text{(insoluble)}}{PbCl_2} + 2HNO_3$$

$$AgNO_3 + HCl = \underset{\text{(insoluble)}}{AgCl} + HNO_3$$

(B) Non-metallic chlorides are usually made by direct combination of the non-metal and chlorine.

$2P + 3Cl_2 = 2PCl_3$ Phosphorus trichloride
$2S + Cl_2 = S_2Cl_2$ Sulphur monochloride

Properties of chlorides

All the chlorides of the common metals, with the exception of those of mercurous HgCl, lead $PbCl_2$, and silver AgCl, are soluble in water.

They react with hot, strong, sulphuric acid, forming sulphates and hydrochloric acid.

$$2M'Cl + H_2SO_4 = M'_2SO_4 + 2HCl$$
$$M''Cl_2 + H_2SO_4 = M''SO_4 + 2HCl$$

M′ and M″ represent atoms of monovalent and divalent metals respectively. If manganese dioxide is added with the sulphuric acid, chlorine is produced.

Ferric chloride, aluminium chloride, and magnesium chloride are partly decomposed by water if their solutions are evaporated to dryness.

$$FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl$$
$$MgCl_2 + 2H_2O = Mg(OH)_2 + 2HCl$$

These chlorides are therefore best made by dry methods.

Solutions of the chlorides react with silver nitrate solution, giving a precipitate of silver chloride which is insoluble in nitric acid.

$$CaCl_2 + 2AgNO_3 = 2AgCl + Ca(NO_3)_2$$
$$ZnCl_2 + 2AgNO_3 = 2AgCl + Zn(NO_3)_2$$

The chlorides of the non-metals are usually not as stable towards heat and towards water as those of the metals. Hydrogen chloride, HCl, carbon tetrachloride, CCl_4, are not decomposed by water, but many of the chlorides of the non-metals are.

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

Phosphorus trichloride — Phosphorous acid

$$2S_2Cl_2 + 2H_2O = SO_2 + 4HCl + 3S$$

Sulphur monochloride — Sulphur dioxide

The chlorides of nitrogen are violently explosive.

PRACTICAL EXERCISES

(1) From mercurous nitrate solution prepare a specimen of mercurous chloride.

(2) From copper carbonate prepare a specimen of cupric chloride.

(3) Dissolve magnesium oxide in hydrochloric acid, evaporate the solution to dryness, and strongly ignite the residue. Try to identify the products.

(4) From tin prepare a crystalline specimen of stannous chloride.

CHAPTER XVI

OXIDES AND OXYACIDS OF CHLORINE

Exp. 109—To prepare a solution of hypochlorous acid

Directions—Pass a stream of chlorine into water in which is suspended calcium carbonate, and filter from the excess of calcium carbonate.

Note the smell of the solution. Try if it will bleach turkey red twill.

Warm a little of the solution with litmus or indigo solution.

Add hydrochloric acid to the solution and test for chlorine.

Exp. 110—To observe the effect of chlorine on a cold solution of caustic potash

Directions—Pass chlorine into a fairly dilute solution of caustic potash, kept cool by water, until the chlorine appears to be no longer absorbed. Then add a few drops more of caustic potash to get rid of free chlorine in the solution.

Notice the smell of the solution. Try whether it will bleach. Add a few drops of a dilute acid to some of the solution and test for chlorine.

To another portion add silver nitrate and nitric acid. Is a chloride present?

Exp. 111—To prepare a sample of bleaching powder

Directions—Place some asbestos loosely in a filter funnel and cover it with a layer of slaked lime. Pass chlorine up the tube of the funnel for half an hour. The experiment should be carried out in a draught chamber.

Shake with water the bleaching powder you obtain, and filter from insoluble matter.

Try the effect of the solution on vegetable dyes, litmus, indigo, turkey red cloth, etc. In each case try the effect of adding a few drops of acid to the solution.

Add caustic soda solution to a solution of lead nitrate until a white precipitate of lead hydroxide is produced. Now add bleaching powder solution in excess, and warm for some time.

Finally warm bleaching powder solution with dilute acid and test for chlorine.

Exp. 112—To prepare potassium chlorate

Directions—Pass chlorine, washed free from hydrochloric acid, into about 50 c.c. of a hot and strong solution of caustic potash, contained in a beaker, until the liquid smells of chlorine. It is advantageous to invert a small filter funnel or thistle funnel in the liquid and pass the chlorine through it. A bigger surface of caustic potash is thus exposed to the chlorine at one time, and there is no danger of the tube becoming choked with crystals.

When the liquid smells of chlorine, concentrate it to about half its bulk and cool. If a good crop of crystals is not obtained, concentrate further. Filter off the crystals. They consist of potassium chlorate mixed with potassium chloride. Potassium chloride is much more soluble than potassium chlorate at ordinary temperatures. Therefore the potassium chlorate can be freed from potassium chloride by recrystallisation. Recrystallise until a crystal dissolved in water gives no precipitate with nitric acid and silver nitrate. When this is the case, the potassium chlorate crystals are pure.

OXIDES OF CHLORINE

There are two well-marked oxides of chlorine, both very unstable.

Chlorine monoxide Cl_2O is prepared by passing dry chlorine over well-cooled, freshly precipitated mercuric oxide.

$$2HgO + 2Cl_2 = HgO.HgCl_2 + Cl_2O$$

Basic mercuric chloride or mercuric oxychloride

The monoxide is a pale yellow gas with a smell somewhat like that of chlorine. It is very explosive.

$$2Cl_2O = 2Cl_2 + O_2$$

It dissolves in water, giving hypochlorous acid HClO.

$$Cl_2O + H_2O = 2HClO$$

Chlorine peroxide, ClO_2, is prepared by adding powdered potassium chlorate, a little at a time, to strong sulphuric acid cooled in a freezing mixture. When the mixture is very gently warmed, the oxide is given off as a gas.

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + H_2O + 2ClO_2$$

Potassium perchlorate

Euchlorine, a mixture of this gas with chlorine, is obtained by warming potassium chlorate with strong hydrochloric acid.

$$4KClO_3 + 12HCl = 4KCl + 6H_2O + 3ClO_2 + 9Cl$$

Chlorine peroxide is a yellow gas, very heavy and very explosive. A hot glass rod introduced into a cylinder of the gas causes it to explode. It is a powerful oxidiser. Its oxidising action may readily be shown by putting a few drops of strong sulphuric acid on a mixture of potassium chlorate and sugar placed on a wooden block. The chlorine peroxide set free ignites the mixture.

Again, phosphorus may be burnt under water by means of this gas. A fragment of phosphorus is dropped on to a few crystals of potassium chlorate placed at the bottom of a cylinder full of water. A few drops of strong sulphuric acid are then run on to the crystals by means of a pipette. The liberated peroxide attacks the phosphorus, which burns in the gas under the water.

HYPOCHLOROUS ACID, HClO

Formation—(1) Dissolve chlorine monoxide in water.

$$Cl_2O + H_2O = 2HClO$$

(2) An easy way to prepare a solution of the acid is to pass chlorine into water containing calcium carbonate.

$$CaCO_3 + H_2O + 2Cl_2 = CaCl_2 + CO_2 + 2HClO$$

Properties—Pure hypochlorous acid, free from water, has not yet been obtained. The solution has a smell somewhat like that of chlorine. It is an even more powerful bleaching agent than chlorine. It reacts with hydrochloric acid, giving chlorine and water.

$$HClO + HCl = H_2O + Cl_2$$

It is a powerful oxidiser. It decomposes on standing, giving chlorine, chloric acid $HClO_3$, oxygen, and water.

The salts of this acid are more stable than the acid. If chlorine is passed into cold caustic potash solution, a chloride and hypochlorite are produced.

$$2KOH + Cl_2 = KCl + KClO + H_2O$$

This solution is not a bleaching agent, but if it is acidified with sulphuric acid, hydrochloric acid and hypochlorous acid are obtained and these react, giving chlorine.

$$KCl + KClO + H_2SO_4 = K_2SO_4 + Cl_2 + H_2O$$

The hypochlorites are good oxidisers. Thus, metallic mercury shaken with sodium hypochlorite solution gives a yellow deposit of mercuric oxide

$$Hg + NaClO = HgO + NaCl$$

A manganese salt, treated with sodium hypochlorite, gives a black precipitate of hydrated manganese dioxide. The manganese is oxidised from the divalent to the tetravalent state.

$$MnCl_2 + NaClO + 2H_2O = MnO_2.H_2O + 2HCl + NaCl$$

When a hypochlorite is treated with dilute hydrochloric acid, chlorine is given off in the cold. The reaction probably takes place in two stages.

$$NaClO + HCl = NaCl + HClO$$
$$HClO + HCl = H_2O + Cl_2$$

BLEACHING POWDER, $CaOCl_2$

Bleaching powder is made on the large scale by passing chlorine into large chambers, the floors of which are covered

with slaked lime. On a small scale it may be made as you have made it. See Exp. III.

$$Ca(OH)_2 + Cl_2 = CaOCl_2 + H_2O$$

Properties—Bleaching powder is an almost white solid which dissolves in water, leaving a slight residue of impurity. When a solution is evaporated *in vacuo*, crystals of calcium hypochlorite $Ca(ClO)_2$ are obtained, and calcium chloride $CaCl_2$ is left in the mother liquor. It would appear, therefore, that bleaching powder consists of a mixture of $Ca(ClO)_2 + CaCl_2$. This is not the case for two reasons. (1) Bleaching powder should, if it contains calcium chloride, be very deliquescent. It is only slightly hygroscopic. (2) Calcium chloride is soluble in alcohol. If freshly made bleaching powder is treated with alcohol and filtered, practically no residue of $CaCl_2$ is obtained on evaporation of the filtrate.

Most probably, bleaching powder has the formula $CaOCl_2$. On treatment with water, it splits up into the two substances calcium chloride and calcium hypochlorite.

$$2CaOCl_2 = CaCl_2 + Ca(ClO)_2$$

Bleaching powder readily gives off chlorine on treatment with dilute acids or with carbon dioxide.

$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2$$
$$CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2$$
$$CaOCl_2 + CO_2 = CaCO_3 + Cl_2$$

It is a powerful oxidising agent. If caustic soda, and afterwards bleaching powder, be added to a solution of lead nitrate, the hydrated lead oxide precipitated by the caustic soda is oxidised by the bleaching powder to lead peroxide.

$$(PbO)_2.H_2O + 2CaOCl_2 = 2PbO_2 + 2CaCl_2 + H_2O$$

Bleaching of cloth is carried out by steeping the cloth successively in bleaching powder solution, dilute acid solution, and then water. The process is repeated until the cloth is bleached.

CHLORIC ACID, $HClO_3$, AND CHLORATES

Chloric acid is obtained in solution by dissolving a known weight of barium chlorate in water, adding the calculated amount of dilute sulphuric acid, and filtering from the precipitated barium sulphate.

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3$$

The solution is a powerful oxidiser and bleacher, and is very unstable. Gently heated, it breaks up into perchloric acid $HClO_4$, oxygen, and chlorine. Its salts are much more stable than the acid. Chlorates, although they contain more oxygen, are more stable than hypochlorites.

Potassium chlorate is readily made by passing chlorine into a hot, strong solution of caustic potash.

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O$$

The crystals of potassium chlorate, which are obtained by concentration and cooling, must be separated from potassium chloride by recrystallisation.

Potassium chlorate, when heated, readily gives up its oxygen. The reaction takes place in two stages.

$$2KClO_3 = KClO_4 + KCl + O_2$$

Potassium perchlorate

When more strongly heated the potassium perchlorate splits up. $KClO_4 = KCl + 2O_2$

The reactions of potassium chlorate with hydrochloric acid and sulphuric acid have already been mentioned.

Owing to the readiness with which it gives up oxygen, potassium chlorate is used in making safety matches, fireworks, etc.

Chlorates of other metals have properties similar to those of potassium chlorate.

PERCHLORIC ACID, $HClO_4$, AND PERCHLORATES

Perchloric acid is made by distilling very small quantities of potassium perchlorate with strong sulphuric acid from a small retort.

$$KClO_4 + H_2SO_4 = KHSO_4 + HClO_4$$

It is a heavy, oily, fuming liquid. It is a powerful oxidiser. If dropped on to dry charcoal, it explodes violently. It sets fire to paper when dropped on it.

Perchlorates are more stable than the chlorates. If potassium chlorate is heated until the molten salt becomes pasty, potassium perchlorate and chloride are formed.

$$2KClO_3 = KClO_4 + KCl + O_2$$

The perchlorate is almost insoluble in cold water. The potassium chloride can therefore be dissolved out by cold water. The undecomposed potassium chlorate can be converted to chloride by heating with strong hydrochloric acid, and the potassium chloride can be dissolved out of the cold product with cold water. The perchlorate is left. Hydrochloric acid has no effect on the perchlorate.

PRACTICAL EXERCISES

(1) From potassium chlorate prepare a specimen of potassium perchlorate.

(2) Find the percentage of oxygen in the specimen of potassium perchlorate obtained in (1).

(3) Find the volume of oxygen at 0° C. and 760 mm. pressure that can be obtained from one gram of potassium chlorate.

(4) Find the percentage loss in weight when potassium chlorate is heated strongly.

CHAPTER XVII

BROMINE, IODINE, AND FLUORINE

Exp. 113—To prepare bromine and investigate its properties

Directions—Fit up the apparatus shown in Fig. 70.

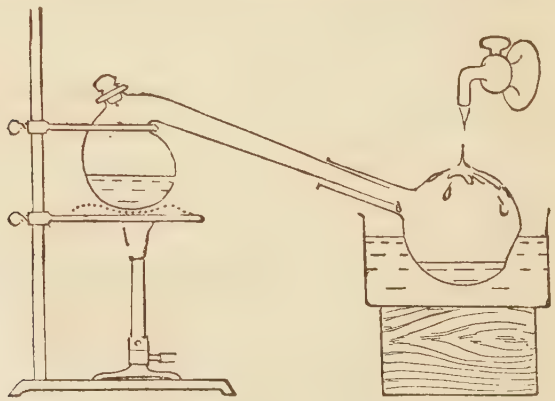


FIG. 70

Into the retort put a mixture of three parts of potassium bromide, one part of manganese dioxide, and add four or five

parts of sulphuric acid which has been diluted with half its own volume of water.

Take care that none of these substances fall into the neck of the retort. Gently warm and collect the bromine in the cooled flask.

(1) Note the colour and smell of the bromine.

(2) Is the bromine heavier or lighter than water? Dissolve some bromine in water and try the effect of the solution on (*a*) litmus, (*b*) turkey red cloth, (*c*) starch solution, (*d*) starch solution mixed with potassium iodide solution.

(3) Try if the bromine will burn.

(4) Drop a small fragment of antimony on two or three drops of bromine placed on a watch glass.

(5) Has the bromine any effect on Dutch metal?

(6) Warm a few drops of bromine in a beaker in a draught chamber, and find out whether bromine vapour will support the combustion of a taper, phosphorus, etc.

Exp. 114—To see if bromine is liberated from a bromide by chlorine

Directions—Make a solution of potassium bromide, and add chlorine water to the solution. Is bromine liberated? Test for the bromine in any way suggested by the last experiment.

Exp. 115—To find out the difference between the action of strong sulphuric acid on a chloride and on a bromide

Directions—Use solid chlorides and bromides. Test for the gases evolved in any ways which occur to you.

Exp. 116—To prepare iodine and investigate its properties

Directions—Proceed exactly as in the preparation of bromine, but use potassium iodide in place of potassium bromide.

(1) Note the colour and smell of the iodine.

(2) Try to make a solution of iodine in (1) water, (2) chloroform, (3) carbon bisulphide.

(3) Make a solution of iodine in potassium iodide solution, and try the effect of the solution on (*a*) litmus, (*b*) turkey red cloth, (*c*) starch solution.

(4) Try whether iodine will burn.

(5) Warm a few crystals of iodine with a small fragment of antimony in a test-tube. Is there any action?

(6) Try whether iodine vapour will support the combustion of a taper, phosphorus, etc.

Exp. 117—To see whether chlorine and bromine set free iodine from iodides

Directions—Make a solution of potassium iodide, and treat portions of it with (*a*) chlorine water, (*b*) bromine water.

Test for iodine in both cases.

Exp. 118—To find out the difference and resemblance in the action of strong sulphuric acid on chlorides, bromides, and iodides

Directions—Use solid salts and test for gases evolved.

Exp. 119—To etch glass by means of hydrofluoric acid

Directions—In a leaden dish place some powdered fluor spar, and cover it with strong sulphuric acid. Very slightly warm the mixture. Cover a piece of flat glass with an even layer of melted wax, and when the wax has solidified, write your name in it with a sharp point, so that the glass is exposed where the letters are to be. Invert the glass plate over the leaden dish, and leave it for a few minutes. Next, scrape off the wax and notice if the glass has been attacked by the gaseous hydrofluoric acid from the dish.

BROMINE. Symbol, Br

History—Discovered by Balard in 1826. He obtained it from the mother liquor left after the crystallisation of the salt from sea water. He called it bromine (Greek, βρῶμος = a stench).

Occurrence—It is never found uncombined in nature. Small quantities of the bromides of potassium, sodium, and magnesium occur in sea water and in some mineral waters. Most of the bromine of commerce is made from the bromide impurities in the carnallite deposits at Stassfurt, in Saxony.

Formation—(1) Bromine is readily prepared by the action of strong sulphuric acid on a mixture of a bromide with

manganese dioxide. The reaction is similar to the reaction by which chlorine was prepared from common salt.

$$2KBr + MnO_2 + 3H_2SO_4 = MnSO_4 + 2KHSO_4 + 2H_2O + Br_2$$

Distil the mixture from a retort into a cooled receiver.

(2) Bromine may be obtained by displacement of the bromine from a bromide by means of chlorine. Chlorine water is added to a solution of a bromide.

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2$$
$$2KBr + Cl_2 = 2KCl + Br_2$$

The bromine can be distilled off and condensed. Excess of chlorine should be avoided, as it combines with bromine, giving bromide of chlorine.

Properties—Atomic weight = 80. Vapour density = 80. Molecular weight = 160. Melting-point = $-7°$ C. Boiling-point, 63° C. Specific gravity, 3.1. 100 grams of water at ordinary temperature dissolve about 3 grams of bromine.

It is a heavy, mobile liquid, deep red in colour. It is the only non-metallic element which is a liquid at ordinary temperature. Bromine vapour is always seen above the liquid in a bottle of bromine, owing to the volatility of bromine at ordinary temperature.

Bromine has a strong, irritating smell. Its vapour attacks the membranes of the nose and throat. Its solution has the colour and smell of the liquid, and, if cooled to 0° C., deposits crystals of a hydrate, $Br_2.10H_2O$.

Its chemical properties are like those of chlorine, but it is less active than chlorine. For instance, it supports combustion less readily than chlorine, bleaches more slowly than chlorine, and does not combine with hydrogen when a mixture of gaseous bromine and hydrogen is exposed to direct sunlight. The mixture of hydrogen and bromine will combine if passed through a red-hot tube.

HYDROBROMIC ACID, HBr

Formation—(1) If a mixture of a bromide and strong sulphuric acid is gently warmed, much of the hydrobromic acid set free reacts with the sulphuric acid, giving bromine and sulphur dioxide.

$$2NaBr + H_2SO_4 = 2HBr + Na_2SO_4$$

The hydrobromic acid then reacts with the sulphuric acid.

$$2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O$$

This method cannot then be used for the preparation of pure hydrobromic acid.

(2) The best method for the preparation consists in dropping bromine on to a mixture of red phosphorus and water. The apparatus used is shown in Fig. 71. A mixture of one part of red phosphorus and two parts of water is placed in the flask, and 7 or 6 parts of bromine are slowly dropped in from the dropping funnel.

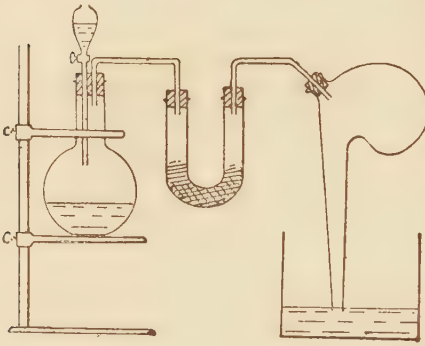


FIG. 71

When all the bromine has been added, the flask may be gently warmed to expel the hydrobromic acid in the solution. The U tube contains red phosphorus, which retains any bromine vapour passing over with the hydrobromic acid. The acid may be collected by downward displacement of air. The inverted retort shown in the figure is used in making a solution of hydrobromic acid. The great solubility of the hydrobromic acid might cause the water in the beaker to be sucked back into the U tube. With the retort present, the water is only sucked up into the bulb, and only air is allowed to pass up.

The reactions taking place in the preparation are—

$$2P + 3Br_2 = 2PBr_3, \quad 2P + 5Br_2 = 2PBr_5$$

The bromides of phosphorus are decomposed by the water.

$PBr_3 + 3H_2O = 3HBr + H_3PO_3$ (Phosphorous acid)

$PBr_5 + 4H_2O = 5HBr + H_3PO_4$ (Phosphoric acid)

(3) Hydrobromic acid can be made by passing a mixture of hydrogen and bromine vapour through a tube containing a spiral of platinum wire heated to redness by an electric current. See Fig. 72.

$$H_2 + Br_2 = 2HBr$$

(4) A solution of hydrobromic acid can be prepared by passing sulphuretted hydrogen into bromine water containing a few drops of liquid bromine. The precipitated sulphur can be removed by filtration.

$$H_2S + Br_2 = 2HBr + S$$

Properties—The properties of hydrobromic acid are so similar to those of hydrochloric acid that it is unnecessary to describe most of them.

It differs from hydrochloric acid in its greater density—it

FIG. 72

is nearly three times as heavy as air—and in being decomposed by sulphuric acid. Hydrochloric acid has no reaction with sulphuric acid.

Chlorine displaces bromine from hydrobromic acid.

$$2HBr + Cl_2 = 2HCl + Br_2$$

A weak or strong solution of hydrobromic acid, boiled for some time, loses water or hydrobromic acid until an acid boiling at 126°, and containing about 47 per cent. of hydrobromic acid, is obtained.

The composition of hydrobromic acid is determined with sodium amalgam in the same way as that of hydrochloric acid.

Bromides are very similar to chlorides. They give off bromine when heated with manganese dioxide and sulphuric acid. They give with silver nitrate solution a yellowish-white precipitate of silver bromide, which is insoluble in nitric acid and sparingly soluble in ammonium hydroxide.

OXYACIDS OF BROMINE

Bromine forms no oxides.

It forms hypobromous acid, HBrO, similar to hypochlorous acid HClO, and bromic acid, $HBrO_3$, similar to chloric acid.

Bromates are formed by the action of solutions of alkalis and bromine, even when the solution of alkali is cold and dilute. Thus—

$$3Br_2 + 6KOH = 5KBr + KBrO_3 + 3H_2O$$

The potassium bromide and bromate can be separated by crystallisation, owing to the greater solubility of the bromide.

The bromates of the alkali metals, when heated, give off oxygen without the formation of an intermediate perbromate.

$$2KBrO_3 = 2KBr + 3O_2$$

IODINE. Symbol, I

History—Iodine was discovered in 1812 by Courtois, who obtained a beautiful violet vapour from the mother liquor left after the crystallisation of the sodium salts contained in the ashes of burnt seaweed. The name is derived from the Greek, ἰοειδής = violet coloured.

Occurrence—It is never found uncombined in nature. It is found in small quantity as sodium iodide in the ashes of the seaweeds *Laminaria digitata* and *Laminaria stenophylla*. These seaweeds are thrown up during storms on the west coast of Scotland and the north coasts of Ireland and France. The inhabitants collect, dry, and burn the weed to obtain the ash, called *kelp*, from which much iodine is made.

Iodine is now mainly made from the sodium iodate which occurs in small quantity in Chili saltpetre.

Formation—(1) Iodine is prepared by distilling a mixture of potassium iodide, manganese dioxide, and sulphuric acid from a retort, and collecting the iodine in a well-cooled receiver.

$$2KI + MnO_2 + 3H_2SO_4 = 2KHSO_4 + MnSO_4 + 2H_2O + I_2$$

(2) It is also obtained by treating a solution of an iodide with chlorine or with bromine.

$$2KI + Cl_2 = 2KCl + I_2, \quad 2KI + Br_2 = 2KBr + I_2$$

Properties—Atomic weight = 127. Molecular weight = 254. Density = 127. Melting-point = 107° C. Boiling-point = 175° C. One gram of iodine dissolves in about 5 litres of water at ordinary temperature.

Iodine is a bluish-black solid which crystallises in shining plates. It vaporises slowly at ordinary temperatures, and has a rather irritating smell.

The colour of iodine vapour changes on heating from violet to deep indigo. The density shows that it contains two atoms in the molecule.

Iodine is almost insoluble in water, but dissolves readily in

chloroform and carbon bisulphide, giving violet solutions. The solutions in alcohol or ether are brownish. It has been suggested that the different colours of the substance are due to different numbers of atoms in the molecules of iodine in the different solutions. Probably the molecules in the brown solutions contain the greater number of atoms, as a solution of iodine in carbon disulphide, if cooled in a freezing mixture, becomes brown.

With starch solution, iodine gives a blue compound. The test is exceedingly delicate. The blue colour disappears on warming, but returns on cooling the solution.

Iodine closely resembles chlorine and bromine in its chemical properties, but it is less active than either. Phosphorus and powdered antimony burn spontaneously in iodine vapour, forming iodides. Mercury warmed with iodine forms mercuric iodide, HgI_2.

HYDRIODIC ACID, HI

Formation—(1) Hydriodic acid cannot be made from an iodide and sulphuric acid, because it reacts with the sulphuric acid, giving iodine and sulphur dioxide.

$$2HI + H_2SO_4 = 2H_2O + SO_2 + I_2$$

It is made by dropping water on to a mixture of red phosphorus and iodine. The apparatus used is identical with that used for the preparation of hydrobromic acid.

$$2P + 5I_2 = 2PI_5$$
$$PI_5 + 4H_2O = H_3PO_4 + 5HI$$

(2) Hydriodic acid can also be obtained by passing a mixture of iodine vapour and hydrogen through a glass tube containing a platinum spiral heated to redness.

$$H_2 + I_2 = 2HI$$

(3) A solution of hydriodic acid can be made by passing sulphuretted hydrogen through water containing finely powdered iodine in suspension. The precipitated sulphur may be removed by filtration or decantation.

$$H_2S + I_2 = 2HI + S$$

Properties—Its properties are very similar to those of hydrochloric acid and hydrobromic acid.

It is, however, more easily split up. A heated wire intro-

duced into the gas will partly split it up into hydrogen and iodine.

Chlorine and bromine set free iodine from the acid.

$$2HI + Cl_2 = 2HCl + I_2$$
$$2HI + Br_2 = 2HBr + I_2$$

A weak or strong solution of hydriodic acid, if boiled, loses water or acid until a solution boiling at 127° and containing about 57 per cent. of hydriodic acid is obtained.

The solution of hydriodic acid, when freshly prepared, is colourless, but it quickly becomes brown owing to the oxidation of the acid by the oxygen of the air.

$$4HI + O_2 = 2H_2O + 2I_2$$

Iodides are made in similar ways to chlorides and bromides. They give iodine if heated with manganese dioxide and strong sulphuric acid, and they give with silver nitrate solution a yellow precipitate of silver iodide, insoluble in nitric acid and insoluble in ammonium hydrate.

$$NaI + AgNO_3 = NaNO_3 + AgI$$

OXIDE AND OXYACIDS OF IODINE

Iodine pentoxide, I_2O_5

This oxide is made by heating iodic acid to 170° C.

$$2HIO_3 = I_2O_5 + H_2O$$

It is a white crystalline solid which dissolves in water, forming iodic acid. It is more stable than the oxides of chlorine. Heated to 300° C. it decomposes into iodine and oxygen.

Iodic acid, HIO_3

This acid can be made by heating iodine with strong nitric acid.

$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O$$

It is a white crystalline solid which gives iodine pentoxide and water when heated.

If iodine is dissolved in alkalis, iodides and iodates are produced.

$$6KOH + 3I_2 = 5KI + KIO_3 + 3H_2O$$

The potassium iodate can be separated by crystallisation.

If heated, potassium iodate splits up into potassium iodide and oxygen.

$$2KIO_3 = 2KI + 3O_2$$

Periodic acid, $HIO_4.2H_2O$

This acid can be obtained by adding iodine to an aqueous solution of perchloric acid.

$$2HClO_4 + 4H_2O + I_2 = Cl_2 + 2HIO_4.2H_2O$$

The acid is a crystalline solid which splits up on heating, according to the equation—

$$2HIO_4.2H_2O = I_2O_5 + 5H_2O + O_2$$

The periodates are fairly stable substances.

FLUORINE. Symbol, F. Atomic weight = 19

History—This exceedingly active element baffled all attempts to isolate it until Moissan, a Frenchman, succeeded in obtaining it in 1886 by electrolysis of liquid hydrofluoric acid containing potassium fluorine in solution.

Occurrence — It occurs in nature in fluor spar CaF_2 (Blue John, Derbyshire spar), cryolite Na_3AlF_6, and apatite $CaF_2.3Ca_3(PO_4)_2$.

Formation — Liquid hydrofluoric acid, containing potassium fluoride in solution, is electrolysed in a U tube made of a platinum and iridium alloy, and the U tube is fitted with fluor spar stoppers carrying platinum-iridium electrodes.

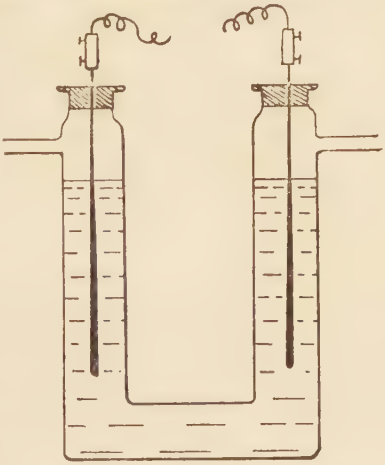


FIG 73

Fig. 73 shows the U tube. The U tube is kept at a temperature of -40 to $-50°$ C. Fluorine is set free at the anode, and hydrogen at the kathode.

The decomposition may be represented—

$$HF.KF = F_2 + H + K$$

The potassium atom then reacts with more hydrofluoric acid, giving another hydrogen atom—

$$HF + K = KF + H$$

The amount of potassium fluoride remains unchanged.

Properties—Fluorine is a colourless gas. It is more active chemically than any other element. It attacks glass, with formation of silicon fluoride SiF_4; decomposes water, giving hydrofluoric acid and ozone; and supports the combustion of nearly all elements, metallic and non-metallic, giving fluorides. Even gold and platinum are attacked by fluorine. In contact with hydrogen, it explodes even in the dark. It does not combine with oxygen.

Its properties, in fact, are those of a very active chlorine.

HYDROFLUORIC ACID, HF

Formation—(1) A solution of the acid is made by distilling a mixture of calcium fluoride and strong sulphuric acid from a leaden retort, and passing the gaseous hydrofluoric acid into water contained in leaden bottles.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

The aqueous solution is sent into the market in gutta-percha bottles.

(2) The acid, free from water, is obtained by distilling acid potassium fluoride from a platinum retort and condensing the acid in a platinum bottle surrounded by a freezing mixture.

$$HF.KF = KF + HF$$

Properties—Anhydrous hydrofluoric acid is a colourless fuming liquid boiling at 17° C.

It is kept in stoppered platinum vessels, because it attacks glass and gutta-percha. Its vapour is poisonous. A drop on the skin produces a painful sore and causes pains throughout the body. The vapour density at 30° C. is 20. This corresponds to the formula H_2F_2. Above 100° C. its vapour density is 10, corresponding to the formula HF.

The action of the gas, or solution, on glass is due to its reaction with the silica of glass.

$$\underset{\text{Silica}}{SiO_2} + 4HF = \underset{\text{Silicon fluoride}}{SiF_4} + 2H_2O$$

It is very soluble in water. The solution dissolves many

COMPARISON OF THE HALOGENS (Fluorine, Chlorine, Bromine, Iodine)

	Fluorine	Chlorine	Bromine	Iodine
Atomic weight .	19	35.5	80.0	127.0
Molecular weight	38	71.0	160.0	254.0
Colour . .	Colourless	Greenish-yellow	Red	Almost black
Smell . .	Pungent, irritating, poisonous	Pungent, irritating, poisonous	Pungent, irritating poisonous	Pungent, irritating, poisonous
Solubility . .	Attacks water	Slight	Slight	Very slight
Action when mixed with hydrogen .	Explodes even in the dark	Explodes in direct sunlight	Combines only when heated strongly	Combines when passed over red-hot platinum
Bleaching action	Destroys most substances	Good bleacher	Fair bleacher	Little bleaching action
Supporter of combustion	Excellent	Excellent	Vapour is a very good supporter of combustion	Vapour is a good supporter of combustion
Compound with hydrogen .	Hydrofluoric acid, HF or H_2F_2; a stable, colourless, fuming, active gas, soluble in water Attacks metals giving fluorides and hydrogen. Etches glass. Not attacked by oxidising agents	Hydrochloric acid, HCl; a colourless, stable, fuming, active gas, very soluble in water. Solution attacks metals giving hydrogen and chlorides With oxidising agents gives chlorine	Hydrobromic acid, HBr; a colourless, fuming, active gas, very soluble in water. Not as stable as hydrochloric acid Solution attacks metals, giving bromides and hydrogen With oxidising agents gives bromine	Hydriodic acid, HI; a colourless, fuming, active gas. Not as stable as hydrobromic acid Solution attacks metals, giving iodides and hydrogen With weak and strong oxidising agents gives iodine
Compounds with oxygen . .	Does not form oxides	Forms two gaseous oxides, Cl_2O and ClO_2, both explosive	Forms no oxides	Forms a solid oxide, I_2O_5, fairly stable
Oxyacids . .	None	HClO, $HClO_2$, $HClO_4$, all unstable Salts more stable than the acids	HBrO, $HBrO_3$, unstable Bromates fairly stable	HIO_3, HIO_4, $2H_2O$, fairly stable Iodates and periodates stable

metals, with evolution of hydrogen and formation of fluorides.

$$2Ag + 2HF = 2AgF + H_2$$

Silver fluoride

Many fluorides are insoluble in water. Those of silver and the alkali metals sodium, potassium, etc., are soluble.

The table on page 197 shows that there is a gradual change in properties, from the very active fluorine to the less active iodine. The hydrogen compounds become less stable from fluorine to iodine.

The oxide of iodine, on the contrary, is more stable than those of chlorine. The properties of bromine and its compounds may be said to be the mean of the properties of chlorine and iodine, just as the atomic weight of bromine is almost the mean of those of chlorine and iodine.

$$\frac{35.5+127.0}{2}=\frac{162.5}{2}=81.25$$

Elements generally can be placed in groups showing between their members general, and often close, relationship in physical and chemical properties. Sulphur, selenium, and tellurium form such a group. Magnesium, zinc, and cadmium; sodium, potassium, rubidium, and caesium are two such groups among the metals. Lothar Meyer and Mendelejeff, in 1869, arranged the elements in order of their atomic weights in such a manner that the eighth element came under the first, the ninth under the second, and so on. They found that similar elements came into the same vertical columns, and they concluded that the properties of the elements were periodic functions of their atomic weights. Their classification is known as the Periodic Classification of the elements. For a detailed account of this classification see Chapter XLVII.

CHAPTER XVIII

SULPHUR AND SULPHURETTED HYDROGEN

Exp. 120—To prepare the allotropic forms of sulphur

Directions—Prepare from ordinary sulphur the different forms of sulphur by the following methods:—

(1) *Rhombic or octahedral sulphur.* Dissolve roll sulphur in carbon bisulphide, filter if necessary, and allow the solution to stand in an evaporating dish. (**Caution**—Carbon bisulphide is very inflammable.)

(2) *Prismatic or monoclinic sulphur.* Melt sulphur in an earthenware crucible, and allow it to cool until a crust forms on the still molten sulphur; make two holes in the crust, pour out the still molten sulphur and remove the crust.

(3) *Plastic sulphur.* Heat sulphur nearly to its boiling-point in some vessel of no value, and pour the molten sulphur into water.

(4) *Amorphous sulphur.* Warm a small quantity of flowers of sulphur with excess of carbon bisulphide, filter, and wash the residue on the paper with more carbon bisulphide. The residue is amorphous sulphur.

Describe the specimens you obtain.

Does each kind of sulphur give the same smell when burnt?

Are all the forms soluble in carbon bisulphide?

Observe any changes which take place when the different forms are allowed to stand for a day or two.

Exp. 121—To determine some of the chemical properties of sulphur

Directions—

(1) Heat sulphur, until it boils, in the vessel used for making plastic sulphur. Into the vapour introduce a piece of copper foil; afterwards put in a few pieces of fine iron wire twisted together and previously heated to redness.

(2) Mix some fine iron filings with flowers of sulphur and heat the mixture strongly in a test-tube. Break the tube and test the powdered product for iron and sulphur.

If iron is present in the metallic state, hydrogen will be given off with dilute sulphuric acid. Smell the gas evolved and try to burn it. If sulphur is present as ordinary sulphur, on warming with carbon bisulphide and evaporating the liquid, crystals of sulphur should be obtained. Try the test.

(3) Fit up an apparatus like that shown in Fig. 74. Into the tube put sulphur, and heat it until it boils. Pass hydrogen through the tube dipping into the molten sulphur. Test the gas issuing from the delivery tube by smell and with filter paper dipped into lead acetate solution.

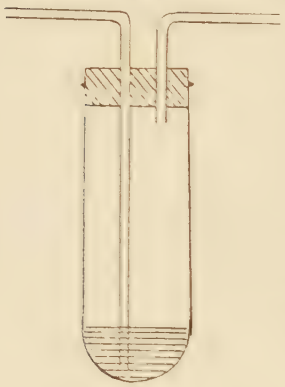


FIG. 74

(4) Heat a small pinch of flowers of sulphur with strong nitric acid for some minutes. Dilute the liquid with water, filter if necessary, and add barium chloride solution. Compare, in as many ways as you can, the precipitate you obtain, with that produced by the addition of barium chloride solution to a very dilute solution of sulphuric acid. Are the precipitates identical?

Exp. 122—To prepare sulphuretted hydrogen and investigate its properties

Note—This preparation, owing to the poisonous nature of the gas, must be carried out in a draught chamber.

Directions.—Prepare sulphuretted hydrogen from ferrous sulphide and dilute sulphuric acid (1 part of acid to 8 or 10 parts of water). Do not warm. Collect the gas by downward displacement of air, and determine its properties in the usual way. Also carry out the following experiments:—

(1) Pass a few bubbles of the gas through solutions of salts of lead, copper, mercury, antimony, stannous, stannic, arsenic, bismuth, and cadmium. In each case notice that the solution becomes acid. Try whether the precipitates are soluble in warm ammonium sulphide solution.

(2) Invert a jar of chlorine over a similar jar of sulphuretted hydrogen, and leave for some minutes. What substances are produced? What does the experiment show?

(3) Mix a jar of dry sulphur dioxide with a larger jar of dry sulphuretted hydrogen. What substances are formed? What does this experiment prove?

(4) Find out whether sulphuretted hydrogen is an oxidising or reducing agent. See oxidation and reduction, page 136.

(5) Try whether the gas will neutralise a dilute solution of caustic soda. Note what happens when you add an acid to the solution you obtain.

(6) Try the effect of the gas on silver, copper, lead, tin.

SULPHUR. Symbol, S

History—Known from the earliest times.

Occurrence—In the free state it occurs in the neighbourhood of volcanoes or in districts which have at one time been volcanic. Large deposits are found in Sicily, Italy, Iceland, and parts of California, China, and India. In some mineral springs it is found in solution as sulphuretted hydrogen, H_2S. Combined with metals, as sulphides, it occurs in large quantities. The chief sulphides are: iron pyrites = FeS_2, copper pyrites = $CuFeS_2$, galena = PbS, zinc blende = ZnS, cinnabar = HgS. As sulphates it occurs as gypsum = $CaSO_4.2H_2O$, heavy spar = $BaSO_4$, kieserite = $MgSO_4$, Epsom salts = $MgSO_4.7H_2O$.

Extraction — The impure sulphur is stacked in a kiln with a sloping floor, air spaces being left. The sulphur is lighted at the bottom. About a third of the sulphur burns and the heat produced melts the rest of the sulphur. The molten sulphur is drawn off into moulds.

The crude sulphur is purified by distillation. The apparatus used is shown in section in Fig. 75.

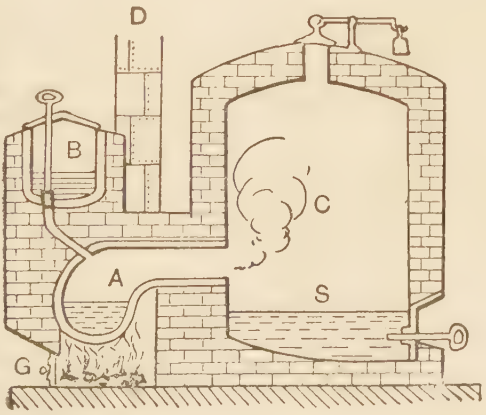


FIG. 75

A = Iron retort
B = Iron pot
C = Large chamber
D = Chimney
G = Grate
S = Molten sulphur

The sulphur is melted in **B**, from which it flows into **A** The sulphur vapour from **A** is condensed in the large brickwork chamber **C**. If the sulphur is distilled slowly, *flowers of sulphur* are obtained. If the distillation is rapid, liquid sulphur collects in the chamber, from which it is drawn off from time to time into moulds.

Formation—(1) One volume of sulphur dioxide reacts with two volumes of sulphuretted hydrogen, producing sulphur.

$$SO_2 + 2H_2S = 2H_2O + 3S$$

This is probably the manner in which the sulphur near volcanoes has been formed.

(2) Sulphur is obtained in a finely divided state on addition of a dilute acid to a solution of a thiosulphate.

$$Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S + H_2O$$

Sodium thiosulphate.

Allotropic forms

Sulphur exists in four well-marked allotropic forms, two crystalline and two amorphous.

Octahedral or rhombic sulphur—This is the form occurring in nature. It is readily made artificially by dissolving sulphur in carbon bisulphide and allowing the solution to evaporate slowly. Rhombic pyramids are obtained. It is owing to the resemblance of these pyramids to octahedrons that rhombic sulphur is often called *octahedral* sulphur. Two forms of these crystals are shown in Fig. 76.

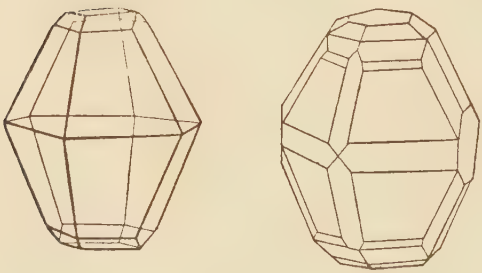


FIG. 76

Rhombic sulphur has a specific gravity of 2.05.

Prismatic sulphur—This variety is obtained by melting sulphur, allowing the molten sulphur to cool until a crust is formed, making a hole in the crust, and pouring out the still liquid sulphur. When the crust is removed, long, yellow, transparent needles of monoclinic or prismatic sulphur are found in the vessel. These needles, on standing for a day or two, become opaque, owing to their transformation into an enormous number of little rhombic crystals. The prismatic form is therefore unstable.

The transformation into rhombic sulphur can be brought about rapidly by putting prismatic crystals into carbon bisulphide. Rhombic sulphur can be made to pass into prismatic sulphur by keeping it at temperatures between 100° and 114° C.

The specific gravity of prismatic sulphur is 1.98.

Plastic sulphur—A good way of obtaining plastic sulphur is to distil sulphur from a small retort, and to allow the sulphur distilling over to drop into water. Fig. 77.

Plastic sulphur is a soft, elastic, amber-coloured solid. It is insoluble in carbon bisulphide. Like prismatic sulphur, it changes to rhombic sulphur on standing, losing its softness, transparency, and elasticity, and becoming hard, brittle, and opaque. The change takes place quickly if the plastic sulphur is worked about with the fingers, or is chewed for a short time.

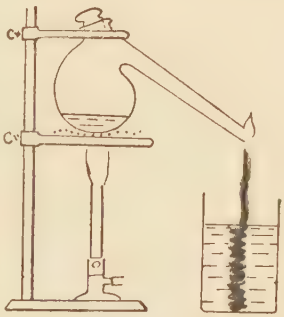


FIG. 77

The specific gravity of this form is 1.95.

Amorphous sulphur—When sulphur vapour is cooled quickly by a cold surface, the greater quantity of the sulphur condenses as octahedral sulphur, but part condenses as amorphous sulphur. If flowers of sulphur which are made in this way are warmed with carbon bisulphide, and the mixture is filtered, white amorphous sulphur is left on the paper. The sulphur precipitated from a solution of a thiosulphate by addition of a dilute acid is also partly amorphous.

Amorphous sulphur is white, non-crystalline, and insoluble in carbon bisulphide. If heated to 100° C. it is changed to ordinary rhombic sulphur.

The specific gravity of this form is 1.95.

General properties of sulphur—Atomic weight = 32. Molecular weight = 64. Vapour density at high temperatures = 32. Melting-point = 114° C. Boiling-point = 448° C. Solubility = nil.

Sulphur is a yellow solid. At temperatures just above the melting-point the liquid is very mobile and reddish in colour.

As the temperature is raised it darkens and becomes more and more viscous, until at 250° C. the liquid is almost black, and so viscous that the vessel containing it can be inverted for a second or two without loss of sulphur. At higher temperatures the liquid again becomes mobile, until at 448° C. it is converted into a dark red vapour. In this vapour, metals such as copper and iron will burn readily, forming sulphides.

$$Fe + S = FeS$$
$$2Cu + S = Cu_2S$$

If finely divided sulphur (4 parts) and iron (7 parts) be mixed and heated, the mixture incandesces, and ferrous sulphide, FeS, is produced.

Sulphur will burn readily in air or oxygen, forming a gas, sulphur dioxide, which has an irritating smell.

$$S + O_2 = SO_2$$

If hydrogen is passed through boiling sulphur, some combination takes place, and traces of sulphuretted hydrogen, which forms lead sulphide (black) with lead acetate paper, are produced.

Sulphur heated with strong nitric acid is oxidised to sulphuric acid, H_2SO_4. The addition of barium chloride to the resulting solution produces a white precipitate of barium sulphate.

$$H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl$$

At high temperatures sulphur vapour has a density of 32. This corresponds to a molecule S_2.

SULPHURETTED HYDROGEN, H_2S

Occurrence—It is one of the gases evolved by volcanoes, and it is sometimes found in solution in mineral waters.

Formation—(1) Small quantities of sulphuretted hydrogen are obtained when hydrogen is passed through boiling sulphur.

$$H_2 + S = H_2S$$

2) Sulphuretted hydrogen is usually prepared by treatment

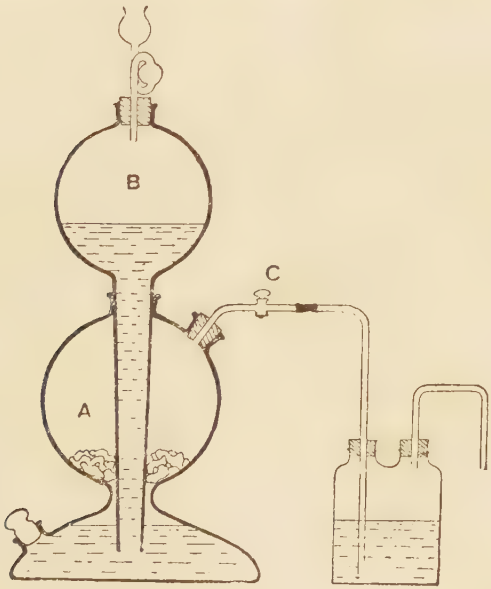


FIG. 78

of ferrous sulphide with cold dilute sulphuric acid or dilute hydrochloric acid in a Kipp's apparatus, Fig. 78.

The ferrous sulphide sticks are put into **A**. Acid (1 to 10 of water) is poured into **B** until, when the tap **C** is open, the acid just covers the ferrous sulphide in **A**. When **C** is closed, the sulphuretted hydrogen fills **A** and forces the acid

up into **B**. By this means the acid is kept out of contact with the sulphide when the apparatus is not in use, and the gas is under a pressure which will force it through liquids.

$$FeS + H_2SO_4 = FeSO_4 + H_2S$$

Ferrous sulphate

The sulphuretted hydrogen should be washed with water to remove mechanically carried particles of acid. The gas obtained by this method always contains traces of hydrogen, due to the action of the acid on minute quantities of metallic iron contained in the ferrous sulphide.

(3) Pure sulphuretted hydrogen is readily made by warming black antimony sulphide with fairly strong hydrochloric acid. The gas must be washed free from hydrochloric acid by passage through a small quantity of water.

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$$

Antimony chloride

Properties—Molecular weight = 34. Density = 17. Solubility at 0° C. = 4.3 volumes of gas in 1 volume of water.

Sulphuretted hydrogen is a colourless gas, with a sweet taste, and a smell resembling that of rotten eggs. It is very poisonous. A bird is killed by an atmosphere containing $\frac{1}{200}$ of the gas. Inhaled in small quantities it gives rise to headache, dizziness, and sickness, and in larger quantities causes death.

The solution has the same taste and smell as the gas. It is acid to litmus. Sulphuretted hydrogen is, however, a very weak acid. It will not completely neutralise caustic soda.

$$NaOH + H_2S = NaSH + H_2O$$

Sodium hydrosulphide

When the solution is exposed to air, the hydrogen is oxidised to water, and sulphur is deposited.

$$2H_2S + O_2 = 2H_2O + 2S$$

Sulphuretted hydrogen burns with a bluish flame, giving, when plenty of air is present, water and sulphur dioxide, but when the air is limited in quantity, sulphur and water. Thus—

(1) $2H_2S + 3O_2 = 2H_2O + 2SO_2$
(2) $2H_2S + O_2 = 2H_2O + 2S$

Mixed with 1½ times its volume of oxygen it forms an explosive mixture. The reaction is shown in equation (1) above.

When mixed with half its volume of sulphur dioxide, sulphuretted hydrogen is decomposed with formation of water and sulphur.

$$2H_2S + SO_2 = 2H_2O + 3S$$

The halogens also decompose the gas, owing to their affinity for hydrogen.

$$H_2S + Cl_2 = 2HCl + S$$
$$H_2S + Br_2 = 2HBr + S$$

Sulphuretted hydrogen is a good reducing agent. If passed into an acidified solution of potassium permanganate the pink colour of the permanganate is destroyed, and sulphur is deposited. It will also reduce ferric chloride to ferrous chloride, and acidified potassium bichromate to a green chromium salt.

$$2KMnO_4 + 5H_2S + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$$
$$K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$
$$2FeCl_3 + H_2S = FeCl_2 + 2HCl + S$$

Sulphuretted hydrogen cannot be dried by means of sulphuric acid. It reduces the acid, giving sulphur dioxide and sulphur.

$$H_2SO_4 + H_2S = SO_2 + 2H_2O + S$$

The gas readily tarnishes metals like silver, tin, and lead. Silver, in the air of towns, becomes coated with a brownish-black film of sulphide, Ag_2S, due to the presence of this gas. Egg-spoons are gilt in order to prevent the blackening of the silver by the gas present in the egg. White-lead paint used for pictures and for ordinary painting is blackened by the gas. The blackening is due to the formation of lead sulphide, PbS.

Sulphuretted hydrogen precipitates metallic sulphides from solutions of salts of many metals. Thus, with hydrochloric acid present in the solution, sulphides of lead, copper, bismuth,

cadmium, mercury, stannous, stannic, arsenic, and antimony are precipitated, the acid of the salt being set free.

$$CuSO_4 + H_2S = CuS + H_2SO_4$$
$$HgCl_2 + H_2S = HgS + 2HCl$$

Other metallic sulphides are insoluble in water, but soluble in hydrochloric acid. These sulphides, although not precipitated by H_2S when hydrochloric acid is present, are precipitated when the solution of the salt is made alkaline by the addition of solutions of ammonium chloride and ammonium hydroxide.

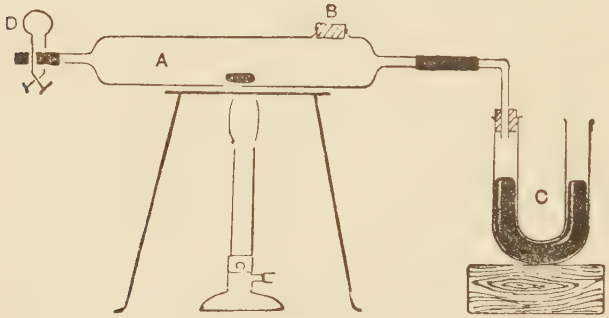


FIG. 79

Sulphides of zinc, manganese, cobalt, and nickel may be prepared in this way.

$$NiSO_4 + H_2S = NiS + H_2SO_4$$
$$ZnCl_2 + H_2S = ZnS + 2HCl$$

The acid set free is at once neutralised by the ammonium hydroxide present.

$$H_2SO_4 + 2NH_4OH = (NH_4)_2SO_4 + 2H_2O$$
$$HCl + NH_4OH = NH_4Cl + H_2O$$

Composition of sulphuretted hydrogen

It is evident, from the fact that some sulphuretted hydrogen can be obtained by passing hydrogen through boiling sulphur, that sulphuretted hydrogen contains only hydrogen and sulphur. The apparatus shown in Fig. 79 can be used to

determine the proportions of these substances present. The tube **A** contains a few pieces of granulated tin, which have been introduced through the aperture **B**. **A** is connected with a U tube **C**. The apparatus is filled with sulphuretted hydrogen by passing the gas through it for ten minutes. The clip **D** is then closed and mercury is poured into the U tube. The pressure is then adjusted to that of the atmosphere by cautiously opening **D**, until the mercury in **C** is level in both limbs. The tin is then heated. It becomes coated with tin sulphide, and hydrogen is set free. When the apparatus is allowed to cool, it is found that the level of the mercury in **C** has not changed.

Therefore, the hydrogen liberated has the same volume as the sulphuretted hydrogen from which it was made.

$\therefore$ 1 volume of sulphuretted hydrogen contains 1 volume of hydrogen.

$\therefore$ 1 molecule of sulphuretted hydrogen contains 1 molecule of hydrogen (Avogadro's Law).

$\therefore$ 1 molecule of sulphuretted hydrogen contains 2 atoms of hydrogen.

$\therefore$ The formula of the gas is H_2S, H_2S_2 or H_2S_x.

The density of sulphuretted hydrogen is 17.

$\therefore$ The molecular weight is 34.

$\therefore$ A molecule of sulphuretted hydrogen contains $34-2=32$ parts of sulphur.

But 32 is the weight of an atom of sulphur.

$\therefore$ The formula of sulphuretted hydrogen is H_2S.

HYDROGEN PERSULPHIDE, H_2S_2

This substance can be prepared by gradually pouring a saturated solution of calcium disulphide (prepared by boiling one part of slaked lime and one part of sulphur with 20 parts of water) into a large excess of hydrochloric acid diluted with its own volume of water. The solution is kept cool and well stirred during the addition of the sulphide. Much sulphur and a small quantity of a yellow oil are precipitated.

The yellow oil is H_2S_2. It may be removed by means of a pipette.

$$CaS_2 + 2HCl = CaCl_2 + H_2S_2$$

Properties—Hydrogen persulphide is a yellow oily liquid of specific gravity 1.75. It bears the same relation to hydrogen sulphide that hydrogen peroxide bears to water.

It forms persulphides corresponding to the peroxides. It acts as a bleaching agent. It is unstable, and readily breaks up into hydrogen sulphide and sulphur, just as hydrogen peroxide breaks up into water and oxygen.

$$2H_2S_2 = 2H_2S + 2S$$
$$2H_2O_2 = 2H_2O + O_2$$

It burns with a blue flame, giving sulphur dioxide and water.

$$2H_2S_2 + 5O_2 = 2H_2O + 4SO_2$$

PRACTICAL EXERCISES

(1) Find the weight of a litre of sulphuretted hydrogen.
(2) From solutions of copper sulphate, stannous chloride, and zinc sulphate, prepare specimens of copper sulphide, stannous sulphide, and zinc sulphide respectively.

CHAPTER XIX

OXIDES AND OXYACIDS OF SULPHUR CARBON BISULPHIDE

Exp. 123—To prepare sulphur dioxide and investigate its properties

Directions—Heat copper turnings with strong sulphuric acid and collect the evolved gas by downward displacement of air. When the gas has begun to come off, very little heat is necessary to maintain the action.

Find out the ordinary properties of the gas, and then carry out the following experiments :—

(1) Make a solution of the gas in about 100 c.c. of water.
(2) Mix a solution of sulphuretted hydrogen with some sulphur dioxide solution.
(3) Try whether the solution will bleach colouring matters,

e.g. rose leaves, litmus, indigo, etc. Try if dilute alkali restores the colour to the bleached materials.

(4) Boil a few c.c. of solution for a minute or two, and add sulphuretted hydrogen solution to find out if all the sulphur dioxide has been expelled.

(5) Find out if sulphur dioxide is a reducing or oxidising agent.

(6) Pour off the liquid remaining in the flask used in the preparation, and try to obtain crystals of copper sulphate from the solid left.

(7) Try to condense some of the gas to liquid by passing it through a U tube, cooled in a freezing mixture of ice and salt. Find the boiling-point of the liquid.

Exp. 124—To find the volume of oxygen contained in sulphur dioxide

Directions—Into a dry test-tube put a piece of sulphur of the size of a pea, and fill the test-tube with oxygen by displacement of air. Next cork the tube tightly with an india-rubber cork fitted with a short glass plug. Wire in the cork. Heat the tube, placed in a nearly horizontal position, until the sulphur lights. When the tube is once more cool, take out the plug under mercury. Does gas escape or does mercury rush in? What conclusion do you draw as to the volume of oxygen contained in sulphur dioxide?

Exp. 125—To determine the properties of sulphuric acid

Directions—

(1) Gradually add about 50 c.c. of strong sulphuric acid to 40 c.c. of water. Stir during the addition. Is there much alteration of temperature? Do you think there is a chemical reaction between water and sulphuric acid?

(2) Put a few c.c. of strong acid in a beaker and weigh it. Allow the beaker to stand in the air for 24 hours and weigh again. What cause can you suggest for the alteration in weight? How could you find out if your suggestion is correct?

(3) Try the effect of cold and hot strong sulphuric acid

on common metals, on oxalic acid, on wood, and on a very strong solution of cane sugar.

Exp. 126—To determine the basicity of sulphuric acid

Directions—

(1) Completely neutralise some sulphuric acid, diluted with three times its volume of water, with caustic soda solution. Do not add an indicator, but take out on a glass rod a drop of the mixture after each addition of caustic soda and touch litmus paper with it. Evaporate down the solution obtained until it crystallises on cooling.

(2) Divide some diluted sulphuric acid into two equal parts. Completely neutralise one part and add the other. Evaporate until the solution crystallises while the temperature is still above 50° C.

(3) Divide some diluted sulphuric acid into three equal parts. Completely neutralise one part and add the other two. Evaporate down the solution to the crystallising point.

Now carefully examine under a strong lens the crystals you have obtained in (1), (2), and (3), and thereby determine whether sulphuric acid can form one, two, or three different sodium salts. What conclusion can be drawn as to the basicity of sulphuric acid ?

Exp. 127—To determine the proportion of $H_2O : SO_3$ in sulphuric acid

Directions—When sulphur trioxide, SO_3, is dissolved in water, a solution possessing all the properties of a dilute solution of sulphuric acid is obtained. Therefore sulphuric acid is a compound of H_2O and SO_3. The ratio H_2O to SO_3 in the pure acid is to be determined. You have learnt that, when a base is neutralised by an acid, a salt and water are obtained. Now, if cupric oxide, CuO, is gently heated with pure sulphuric acid, the water formed is driven off and copper sulphate remains. By no method can any hydrogen be obtained from anhydrous copper sulphate. Therefore all the hydrogen in sulphuric acid has been driven off as water. This water driven off therefore represents the water which was combined with the sulphur dioxide in the sulphuric acid.

The increase in weight of the copper oxide, when converted into sulphate, will represent the weight of sulphur trioxide which was combined with the water driven off.

Put about 10 grams of cupric oxide into a small porcelain dish, and heat to low redness over a small bunsen flame to dry the oxide. When the dish is cool, weigh it. Weigh a small beaker containing one or two c.c. of pure strong sulphuric acid. Pour 10 or 12 drops of sulphuric acid from the beaker on to the copper oxide, and weigh the beaker again. Heat the copper oxide and sulphuric acid in the steam oven for half an hour, and then over a very small bunsen flame placed several inches below the dish. Gradually increase the temperature until the bottom of the dish is dull red. Weigh again. Heat and re-weigh until the weight is constant. *Note—If white fumes come off during the heating, you are heating too strongly.* Calculate the weight of water combined with sulphur trioxide in sulphuric acid.

An experiment gave the following results :—

Weight of dish and CuO = 25.62 gms. Weight of beaker and H_2SO_4 = 47.67 gms. Weight of beaker and residual H_2SO_4 = 45.79 gms. Final weight of dish, residual CuO, and $CuSO_4$ = 27.14 gms.

∴ Weight of H_2SO_4 used = 1.88 gms. ∴ Weight of SO_3 in 1.88 gms. of H_2SO_4 = 27.14 − 25.62 = 1.52 gms.

∴ Weight of H_2O in H_2SO_4 = 1.88 − 1.52 = .36 gm.

$$\therefore \frac{\text{Weight of } SO_3}{\text{Weight of } H_2O} = \frac{1.52}{.36} = \frac{80}{18.9}.$$ But $SO_3 : H_2O$ as 80 : 18.

∴ Acid contains one SO_3 combined with one H_2O.

Ferric oxide may be used in place of cupric oxide.

Exp. 128—To prepare a specimen of crystalline ferrous sulphate from iron filings

Directions—Use excess of iron filings and use sulphuric acid diluted with 4 or 5 times its volume of water. Filter from excess of iron and concentrate the solution in a flask until a specimen of the solution crystallises when taken out and cooled in a test-tube. Ferrous sulphate solution is readily oxidised to ferric sulphate by the oxygen of the air. The solution should therefore be exposed to the air as little as possible. As long as the flask is filled with steam during the concentration, the air can have little effect.

The air may be excluded from the flask during solution and crystallisation by use of the bunsen valve, shown in Fig. 80. The bunsen valve consists simply of an india-rubber tube with a V-shaped slit **A** cut in it. Gas can escape from **A**, but no air can enter the flask because **A** is closed as soon as the pressure inside the flask is less than that of the atmosphere. Dry your specimen of ferrous sulphate by pressing it between sheets of blotting paper, and test a portion of it for ferric salt by addition of potassium sulphocyanide solution. If ferric salt is present, a red coloration will be produced.

FIG. 80

Exp. 129—To test for sulphates

Directions—

(1) To a solution of a sulphate add dilute hydrochloric acid and barium chloride solution. The formation of a white precipitate of barium sulphate, insoluble in water and acids, indicates the presence of a sulphate.

(2) Mix a small quantity of a solid sulphate with its own bulk of sodium carbonate, and heat the mixture on charcoal before the blow-pipe. Place the substance you obtain on a silver coin and moisten with water. A brownish-black stain of silver sulphide on the coin indicates the presence of a sulphate. The stain is due to the reduction of the sulphate to sulphide by the charcoal, the reaction of the sulphide with sodium carbonate to give sodium sulphide, and the reaction of the solution of sodium sulphide with the silver to give silver sulphide, Ag_2S.

SULPHUR DIOXIDE, SO_2

Occurrence—It is present among the gases emitted by volcanoes. Coal contains sulphur compounds, which burn at the same time as the coal, and produce sulphur dioxide. The gas is therefore present to a slight extent in the air of towns.

Formation—(1) Sulphur dioxide is formed when sulphur is burnt in air. Made in this way it appears misty, owing to the formation of small quantities of sulphur trioxide.

$$S + O_2 = SO_2$$

(2) It is usually prepared in the laboratory by heating copper turnings with strong sulphuric acid. Fig. 81.

The wash-bottle **B** contains a small quantity of water to wash the gas from traces of sulphuric acid carried over. The gas is collected by downward displacement of air.

If dry gas is required, a second wash-bottle containing strong sulphuric acid must be used.

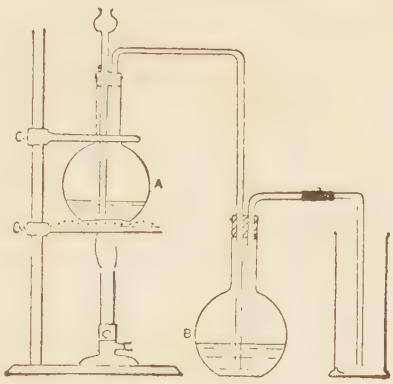


FIG. 81

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$

The slimy, blackish residue contains sulphides of copper as well as copper sulphate, so that the reaction is not quite as simple as that indicated by the equation.

Mercury, lead, silver, carbon, or sulphur may be substituted for copper, but copper gives the best results.

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2$$
$$Pb + 2H_2SO_4 = PbSO_4 + 2H_2O + SO_2$$
$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O$$
$$S + 2H_2SO_4 = 3SO_2 + 2H_2O$$

(3) Sulphur dioxide is also obtained on adding dilute sulphuric acid to a sulphite or thiosulphate.

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + SO_2 + H_2O$$

Sodium sulphite

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + SO_2 + S + H_2O$$

Sodium thiosulphate

Properties—Density = 32. Molecular weight = 64. Melts at −76° C. Boils at −10° C. One c.c. of water at 0° C. dissolves about 80 c.c. of sulphur dioxide.

Sulphur dioxide is a colourless gas with the irritating smell of burning sulphur. It is more than twice as heavy as air.

It is readily soluble in water, and the solution smells like the gas. If boiled for some time the solution loses all trace of the gas.

The solution is acid to litmus, and behaves towards alkalis, etc., as if it contained sulphurous acid, H_2SO_3.

The gas can readily be liquefied by passing it through a tube cooled below $-10°$ C. in a freezing mixture. The liquid can also be obtained by subjecting the gas to a pressure of 5 or 6 atmospheres at ordinary temperatures. Liquid sulphur dioxide is sent into market in glass syphons. It is a colourless liquid which solidifies at $-76°$ to an ice-like mass. If some of the liquid is thrown on water, some of the water is frozen. This is due to the rapid evaporation of part of the sulphur dioxide. The heat absorbed in this evaporation is supplied by the water, which is thus frozen. The ice formed contains some of the solid compound $H_2SO_3.8H_2O$.

Sulphur dioxide will not burn or support the combustion of a taper, sulphur, carbon, etc. Sodium will burn in the gas, and tin and finely divided iron can also be made to burn in it. Sulphides and oxides of the metals are formed.

If sulphur dioxide is passed over dry lead peroxide, the lead peroxide becomes incandescent and lead sulphate is produced.

$$\underset{\text{Lead peroxide}}{PbO_2} + SO_2 = \underset{\text{Lead sulphate}}{PbSO_4}$$

Sulphur dioxide is a good bleaching agent when water is present. It bleaches by its absorption of oxygen, not by oxidation as chlorine does. The hydrogen set free forms colourless compounds with the colouring matter.

$$\left\{\begin{array}{l} SO_2 + H_2O = H_2SO_3 \\ H_2SO_3 + H_2O = H_2SO_4 + 2H \end{array}\right.$$

In some cases the sulphur dioxide itself forms colourless compounds with the colouring matter.

It is used for bleaching substances which would be injured by chlorine. Silk, straw, wool, sponges, etc., are often bleached by it. The original colour, in many cases of bleaching by sulphur dioxide, can be restored by the addition of weak alkalis. Sponges or flannel trousers become yellow after being several times washed. This is owing to the

restoration of the original colour of the material by the alkali present in soap.

Sulphur dioxide solution, on standing for some time exposed to air, becomes partly oxidised to sulphuric acid.

$$2H_2SO_3 + O_2 = 2H_2SO_4$$

In consequence of the ease with which it combines with oxygen, sulphur dioxide is an excellent reducing agent. It reduces ferric salts to ferrous, acidified potassium bichromate to a chromium salt, potassium permanganate to a manganese salt, etc.

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$
$$Fe_2(SO_4)_3 + SO_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$$

Sulphur dioxide is sometimes used as an "antichlor," that is, for removing chlorine from substances bleached by that gas. The chlorine oxidises it to sulphuric acid.

$$SO_2 + 2H_2O + Cl_2 = H_2SO_4 + 2HCl$$

It is also used as a disinfectant, as it destroys many germs which cause decay or disease. Rooms are sometimes disinfected after illness by burning sulphur in them. The casks in which wine is stored are often fumed with sulphur dioxide to prevent the spoiling of the wine by the acetic acid ferment, and to prevent the growth of certain fungi.

FIG. 82

Composition of sulphur dioxide

Sulphur dioxide can be made by burning sulphur in oxygen. Therefore it contains only sulphur and oxygen. You have found that it contains its own volume of oxygen. An apparatus for proving this is shown in Fig. 82.

The U tube is partly filled with mercury, and the air in the bulb is displaced with oxygen. The stopper, carrying two wires, is then put in. One of the wires supports a bone ash boat, and it is connected to the other by means of a loop of thin platinum wire. A piece of sulphur is placed in the

boat and ignited by heating the loop of platinum wire to redness by means of an electric current. The sulphur burns in the oxygen, giving sulphur dioxide. When the apparatus is cold, no change from the original volume is noticed.

Therefore sulphur dioxide contains its own volume of oxygen.

∴ 1 molecule of sulphur dioxide contains 1 molecule of oxygen (Avogadro's Law).

∴ 1 molecule of sulphur dioxide contains 2 atoms of oxygen.

∴ The formula of sulphur dioxide is SO_2, S_2O_2, or S_xO_2.

The density of sulphur dioxide is 32.

∴ The molecular weight is 64.

∴ Sulphur dioxide contains $64-32=32$ parts of sulphur.

But 32 is the weight of one atom of sulphur.

∴ The formula for sulphur dioxide is SO_2.

SULPHUROUS ACIDS AND SULPHITES

Sulphurous acid is only known in solution and combined with water. If a solution of sulphur dioxide is cooled down to 0° C., a solid hydrate, $H_2SO_3.8H_2O$, crystallises out.

The solution acts like a dibasic acid. Thus, if caustic soda is added to excess of the solution of sulphur dioxide, acid sodium sulphite is produced.

$$H_2SO_3+NaOH=NaHSO_3+H_2O$$

If, however, excess of caustic soda is used, normal sodium sulphite is formed.

$$H_2SO_3+2NaOH=Na_2SO_3+2H_2O$$

The normal sulphites have no smell. Only those of the alkali metals, sodium, potassium, etc., are readily soluble in water. Acid sulphites smell of sulphur dioxide.

Sulphites are readily detected by the evolution of sulphur dioxide on treatment with a dilute acid.

$$Na_2SO_3+H_2SO_4=Na_2SO_4+SO_2+H_2O$$
$$NaHSO_3+H_2SO_4=NaHSO_4+SO_2+H_2O$$

SULPHUR TRIOXIDE, SO_3

Formation—(1) Sulphur trioxide can be prepared by passing a mixture of dry sulphur dioxide and oxygen through a tube

containing platinised asbestos* heated to redness, and condensing the compound produced in a well-cooled flask.

The asbestos, hard glass tube, and flask should be thoroughly dried. If a crystalline specimen of sulphur trioxide is wanted, a flask with the neck drawn out to a narrow tube is used as a receiver. The mouth of the flask is packed loosely with asbestos, to prevent any sulphuric acid, formed by the

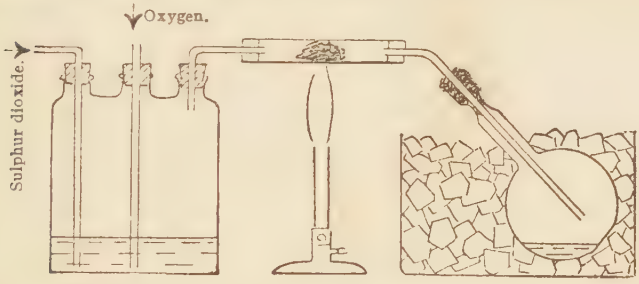


FIG. 83

absorption of water vapour from the air by the trioxide, from running back into the flask. As soon as sufficient sulphur trioxide has been collected, the flask is sealed off.

$$2SO_2 + O_2 = 2SO_3$$

The receiver should not be cooled below $-10°$ C., or sulphur dioxide will also be condensed.

(2) An easy way to obtain sulphur trioxide is to distil fuming sulphuric acid (Nordhausen sulphuric acid) from a retort.

$$H_2S_2O_7 = H_2SO_4 + SO_3$$

The trioxide distils over, and is collected in a well-cooled receiver.

Properties—Vapour density = 40. Molecular weight = 80. Melts at 14 8°. Boils at 46° C.

Sulphur trioxide is a white crystalline solid. It melts at 14.8° and boils at 46° C. A specimen contained in a dry sealed flask gradually fills the flask with long silky needles. These needles do not melt, but pass directly from the solid to the gaseous state. There are therefore two distinct forms of sulphur trioxide.

* Platinised asbestos is asbestos impregnated with finely divided platinum. It is made by strongly heating asbestos which has been dipped into a solution of platinic chloride.

Sulphur trioxide rapidly absorbs moisture from the air and forms sulphuric acid.

$$H_2O + SO_3 = H_2SO_4$$

When dry it has no action on litmus. If passed over basic oxides, such as lime CaO or baryta BaO, it combines with them vigorously, forming sulphates.

$$SO_3 + BaO = BaSO_4$$

If passed through a red-hot tube, it is spilt up into sulphur dioxide and oxygen.

$$2SO_3 = 2SO_2 + O_2$$

Two volumes of sulphur trioxide vapour give two volumes of sulphur dioxide and one volume of oxygen. From this fact, together with the fact that the vapour density is 40, the formula SO_3 for the compound is deduced.

SULPHURIC ACID, H_2SO_4

Formation—(1) When sulphur trioxide is dissolved in water, sulphuric acid is formed.

$$SO_3 + H_2O = H_2SO_4$$

(2) If sulphur dioxide solution is allowed to stand in air it takes up oxygen, and forms sulphuric acid.

$$SO_2 + H_2O + O = H_2SO_4$$

(3) Sulphuric acid is manufactured by oxidation of sulphur dioxide by means of oxides of nitrogen. Water, in the form

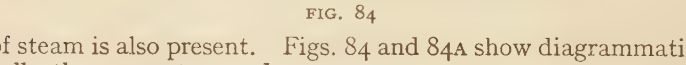


FIG. 84

of steam is also present. Figs. 84 and 84A show diagrammatically the apparatus used.

(*a*) **A** are kilns in which iron pyrites is burned, or, when pure sulphuric acid is required, ovens in which brimstone (sulphur ore) is burned.

With pyrites the chemical action is—

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

With brimstone the chemical action is—

$$S + O_2 = SO_2$$

(*b*) The hot sulphur dioxide, mixed with much air, passes

the mixture is partly removed and partly diluted. The gases then pass up towers down which descend sprays of water, and afterwards up a tower down which trickles strong sulphuric acid. In this way the gases are further purified and dried They then enter the contact chamber, which contains small perforated shelves covered with a layer of platinised asbestos or of ferric oxide.

The best temperature for the combination of the gases is 350° C. Heat to start the reaction is supplied by gas jets, but the combination of the sulphur dioxide and oxygen of the air produces the heat necessary to maintain the temperature.

The sulphur trioxide produced is absorbed by 97 or 98 per cent. sulphuric acid, Nordhausen sulphuric acid, commercially known as "oleum," being formed. If ordinary sulphuric acid is required, the concentration of the acid in the absorbing apparatus is kept at 97 or 98 per cent. by running in water.

$$SO_3 + H_2SO_4 = H_2S_2O_7 \text{ (Nordhausen sulphuric acid)}$$
$$H_2S_2O_7 + H_2O = 2H_2SO_4$$

Preparation of sulphuric acid in the laboratory

A flask of capacity about 6 or 8 litres is fitted with a cork carrying five tubes. See Fig. 85. Into the flask is passed sulphur dioxide, steam, nitric oxide, and oxygen. If only a small quantity of steam is at first sent in, chamber crystals can be obtained on the sides of the flask. When steam is again driven in, the crystals react with it, and give oxides of nitrogen and sulphuric acid.

$$2HNOSO_4 + H_2O = 2H_2SO_4 + NO_2 + NO$$

If the stream of oxygen be stopped for some time, the gases in the flask gradually become colourless, owing to the conversion of all the nitrogen peroxide into nitric oxide. When oxygen is again passed, the colourless nitric oxide is once more converted into red nitrogen peroxide.

$$2NO + O_2 = 2NO_2$$

In this way the main changes taking place in the manufacture of sulphuric acid can be imitated on a small scale.

Properties—Density = 24.5. Molecular weight = 98. Melting-point = 10.5° C. Boiling-point = 338° C.

Sulphuric acid is a heavy, oily liquid. If cooled to 0°,

colourless crystals of sulphuric acid, containing 100 per cent. of sulphuric acid, separate out. These crystals melt at 10.5° C.

When warmed, the strongest sulphuric acid gives off sulphur trioxide until it contains 1.5 per cent. of water. It then distils unchanged at 338° C.

Sulphuric acid has a great affinity for water. It is therefore an excellent drying agent for gases which are not attacked by it. When it is mixed with water, much heat is given out. Definite hydrates, having the composition $H_2SO_4.H_2O$ and $H_2SO_4.4H_2O$, have been obtained from its solution.

Sulphuric acid will take out the elements of water from many organic substances containing hydrogen and oxygen. Thus oxalic acid, when warmed with strong sulphuric acid, gives off carbon dioxide and carbon monoxide.

$$C_2H_2O_4 - H_2O = CO_2 + CO$$

If a strong solution of cane sugar, $C_{12}H_{22}O_{11}$, is placed in a beaker and mixed with strong sulphuric acid, water is taken out from the sugar and a mass of carbon, inflated with steam and sulphur dioxide, is set free. The mass swells up and fills the beaker. In a similar way wood is charred and flesh is corroded by the strong acid.

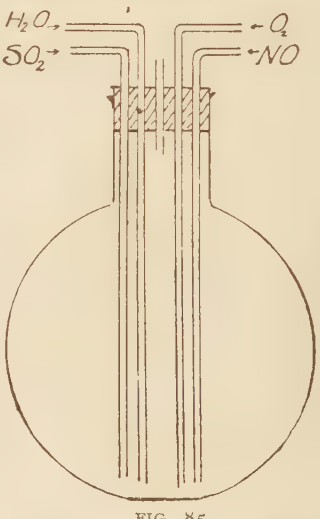


FIG. 85

Dilute sulphuric acid with copper, lead, and tin has practically no action ; with zinc and iron, hydrogen is evolved and zinc sulphate and ferrous sulphate are formed.

$$Fe + H_2SO_4 = FeSO_4 + H_2$$

Most metals, when heated with strong sulphuric acid, give sulphur dioxide.

$$Zn + 2H_2SO_4 = ZnSO_4 + 2H_2O + SO_2$$

Sulphuric acid is a dibasic acid. It therefore forms two series of salts, normal and acid.

$$NaOH + H_2SO_4 = \underset{\text{Acid sodium sulphate}}{NaHSO_4} + H_2O$$

$$2NaOH + H_2SO_4 = \underset{\text{Normal sodium sulphate}}{Na_2SO_4} + 2H_2O$$

Composition of sulphuric acid

Sulphuric acid contains only sulphur, oxygen, and hydrogen, because it can be made by dissolving sulphur trioxide in water. The experiment with cupric oxide and strong sulphuric acid proves that sulphur trioxide combines with water in the proportion $SO_3 : H_2O$. Therefore the formula must be $(H_2SO_4)_x$.

The molecular weight of a substance can usually be found from its density. The density of sulphuric acid is, however, only 24.5. The molecular weight, therefore, should be 49. H_2SO_4 is the simplest possible formula for the acid. But the weights of the atoms in the formula H_2SO_4 add up to 98. Evidently the density is abnormal, that is, the sulphuric acid must be dissociated on conversion to vapour. It is split up into sulphur trioxide and water.*

The density of a mixture of equal volumes of sulphur trioxide vapour and water vapour will be the mean of the densities of these substances.

Density of $SO_3 = \frac{32+48}{2} = 40$. Density of $H_2O = \frac{2+16}{2} = 9$.

Mean of the densities of SO_3 and $H_2O = \frac{40+9}{2} = 24.5$.

24.5 is the density actually found for the vapour of sulphuric acid.

* The dissociation of sulphuric acid into sulphur trioxide and water can be shown by heating sulphuric acid above its boiling-point for some time in a flask provided with a neck drawn out to a capillary tube. Water vapour has a density of 9. Sulphur trioxide vapour has a density of 40. Therefore water vapour diffuses from the capillary much faster than the sulphur trioxide. The residual acid in the flask consequently contains a larger proportion of sulphur trioxide than the original sulphuric acid.

Now if $x=2$ in the formula $(H_2SO_4)_x$, the formula for the acid would be $H_4S_2O_8$. As all the hydrogen in sulphuric acid can be replaced by metals, there would be four classes of salts. The four sodium salts would be $NaH_3S_2O_8$, $Na_2H_2S_2O_8$, $Na_3HS_2O_8$, and $Na_4S_2O_8$. There are, however, only two series of salts. Presumably, therefore, there are only two atoms of hydrogen in the molecule of sulphuric acid.

$\therefore$ The formula is H_2SO_4.

Sulphates and isomorphism

Sulphates may be readily prepared by solution of a metal, metallic oxide, hydroxide, or carbonate in dilute sulphuric acid. Most sulphates are soluble in water; those of lead, barium, strontium are insoluble in water; that of calcium is only slightly soluble.

The *vitriols* form an important class of sulphates. These salts crystallise with 7 molecules of water of crystallisation, and give off 6 molecules at 100° C. The residual molecule of water, which is sometimes called *water of constitution*, is given off at temperatures above 200° C.

Examples of these sulphates are—

$MgSO_4.7H_2O$	Magnesium sulphate
$ZnSO_4.7H_2O$	Zinc sulphate
$FeSO_4.7H_2O$	Iron sulphate (green vitriol)

Copper sulphate, blue vitriol, contains only 5 molecules of water, four of which it gives up at 100° C.

The *alums*, of which there are about 70, are double sulphates. These are of the type $M_2'SO_4.M'''(SO_4)_3.24H_2O$ where M′ = a monovalent metal such as potassium or sodium and M‴ = a trivalent metal such as iron, aluminium, chromium, or manganese. Thus, ordinary alum or potash alum has the formula $K_2SO_4.Al_2(SO_4)_3.24H_2O$, and chrome alum has the formula $K_2SO_4.Cr_2(SO_4)_3.24H_2O$.

The alums furnish excellent examples of **isomorphism.** Salts are said to be isomorphous when they crystallise in the same form. If salts are truly isomorphous, a crystal of one, suspended in a saturated solution of the other, will grow. owing to the deposition of the second salt on the first. This is known as *overgrowth*. For example, if a crystal of the

deep red chrome alum is suspended in a saturated solution of ordinary alum and left for some time, a deposit of clear, colourless alum will form round the chrome alum crystal. The nucleus of chrome alum can be seen through the outer coating of potash alum

Again, if salts are truly isomorphous, a crystal deposited from a mixed solution of the two salts will contain both substances. This is known as the formation of *mixed crystals*. For example, a crystal deposited from a mixed solution of chrome alum and ordinary alum would, on analysis, be found to contain both chromium and aluminium.

OTHER ACIDS OF SULPHUR

Besides sulphurous acid and sulphuric acid, other acids of sulphur exist. Of these the most important are thiosulphuric acid, $H_2S_2O_3$, and pyrosulphuric acid, $H_2S_2O_7$.

Sodium thiosulphate, $Na_2S_2O_3$, is an important salt of thiosulphuric acid. It can be made by warming flowers of sulphur with a solution of sodium sulphite.

$$Na_2SO_3 + S = Na_2S_2O_3$$

Thiosulphates react with dilute acids with evolution of sulphur dioxide and deposition of sulphur.

$$Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S + H_2O$$

Sodium thiosulphate is the "hypo" of the photographer. He uses a solution of this salt for *fixing*, an operation which consists in dissolving out silver salts from negatives and prints which have been developed or exposed to sunlight. Thus—

$$AgCl + Na_2S_2O_3 = \underset{\text{(soluble in water)}}{AgNaS_2O_3} + NaCl$$

Sodium thiosulphate solution is useful also in volumetric analysis for the titration of solutions of iodine, with which it reacts according to the equation—

$$2Na_2S_2O_3 + I_2 = \underset{\text{tetrathionate}}{Na_2S_4O_6} + 2NaI$$

Pyrosulphuric acid (*Nordhausen sulphuric acid or fuming sulphuric acid*), $H_2S_2O_7$

This acid is made by distilling ferrous sulphate, which has previously been heated until it contains only one molecule of water of crystallisation.

The acid condenses as a heavy, colourless, fuming liquid. When cooled it solidifies to a crystalline mass. The crystals melt at 35° C. When heated strongly, sulphur trioxide is driven off and sulphuric acid is left.

$$H_2S_2O_7 = H_2SO_4 + SO_3$$

It forms a series of stable salts.

CARBON BISULPHIDE, CS_2

Formation—Carbon bisulphide is made by passing sulphur vapour through red-hot carbon. The vapour of the carbon bisulphide is condensed to liquid by means of a long Liebig condenser.

$$C + S_2 = CS_2$$

Properties—It is a colourless, mobile liquid, which boils at 46° C. The vapour of carbon bisulphide can be ignited by means of a glass rod heated to 120° C. It burns with a blue flame, forming carbon dioxide and sulphur dioxide.

$$CS_2 + 3O_2 = CO_2 + 2SO_2$$

If, therefore, the vapour of carbon bisulphide is mixed with three times its volume of oxygen, it forms an explosive mixture.

When pure, carbon bisulphide has a sweet and not unpleasant smell. Very few substances, however, have a worse smell than impure carbon bisulphide. Its vapour is poisonous.

Carbon bisulphide is an excellent solvent for phosphorus, iodine, sulphur, india-rubber, and many fats and oils.

SELENIUM AND TELLURIUM

These somewhat rare elements closely resemble sulphur. Selenium, like sulphur, occurs in several allotropic modifications—(1) crystalline, (2) plastic, (3) amorphous. Tellurium is metallic in appearance.

Both elements form hydrides, H_2Se, H_2Te, corresponding to H_2S. They also form oxides and acids, SeO_2, TeO_2, TeO_3, H_2SeO_3, H_2TeO_3, H_2SeO_4, H_2TeO_4, closely allied to the corresponding compounds of sulphur.

The atomic weight of selenium, 79, is the mean of those of sulphur, 32, and tellurium, 126. The properties of selenium and the properties of its compounds are similarly the mean of those of sulphur and tellurium.

PRACTICAL EXERCISES

(1) From copper, zinc, iron, lead, prepare specimens of copper sulphate, zinc sulphate, ferric sulphate, and lead sulphate respectively.

(2) Find the weight of sulphuric acid required to dissolve one gram of zinc. A standard solution of caustic soda is provided.

(3) Prepare a crystalline specimen of sodium thiosulphate.

(4) Make a supersaturated solution of sodium thiosulphate.

(5) Crystallise a solution of chrome alum. Pick out a well-shaped crystal and suspend it by means of a piece of cotton or horse hair in a glass jar in a cold saturated solution of chrome alum. Leave for some days, and then free the cotton from any small crystals, and filter the solution if any crystals of alum have formed at the bottom of the jar. Leave again, and free the cotton and jar from crystals until you have grown a fairly large crystal. Next suspend the crystal of chrome alum in a saturated solution of ordinary alum, and try to grow a thick coat of ordinary alum on the crystal of chrome alum.

CHAPTER XX

NITROGEN—THE ATMOSPHERE—AMMONIA

Exp. 130—To prepare nitrogen from the air

Directions—Prepare nitrogen by burning phosphorus in air contained in a bell jar or gas jar inverted in water. Allow the fumes of phosphorus pentoxide to dissolve in the water, and then determine as many properties of the nitrogen as you can.

Exp. 131—To prepare nitrogen from ammonium chloride

Directions—First Method—Finely powder about 25 grams of potassium bichromate, and mix the powder thoroughly with 10 grams of ammonium chloride. Heat the mixture in a hard glass tube connected to a wash-bottle containing pieces of glass or pumice moistened with water. This wash-bottle is a scrubber to remove fumes of ammonium chloride from the nitrogen produced. Collect the nitrogen over water and investigate its properties.

Second Method—Into a flask fitted with cork and delivery tube put about 15 grams of ammonium chloride, 15 grams of sodium nitrite, and about 60 c.c. of water. Warm gently until the action begins, remove the flame, and collect the nitrogen over water. If the action becomes too rapid, cool the flask in a water bath containing cold water.

Exp. 132—To prove experimentally that nitrogen, oxygen, carbon dioxide, and water vapour are present in air

Directions—Make use of the following information :—

Fused calcium chloride deliquesces in presence of water vapour.

Carbon dioxide turns lime-water milky. Oxygen turns freshly made pyrogallic acid solution brown, and forms oxides with combustibles. Nitrogen is almost insoluble in water, and does not support combustion.

Carry out any experiments which seem to you to prove the presence in air of the above-mentioned substances.

Exp. 133—To determine the proportions of oxygen, nitrogen, and carbon dioxide in breathed-out air

Directions—To a piece of copper wire quickly fasten about one inch of a stick of caustic soda. Wash your fingers immediately to get rid of the corrosive caustic soda.

Fill a 100 c.c. measuring tube with water and invert it in a trough. Into the tube blow air from your lungs until you have introduced about 100 c.c. of respired air. Quickly level the tube and read the volume of the air. Next introduce the caustic soda on the wire, and leave for five minutes. Read the volume, and leave for a second five minutes. If there is a further diminution of the volume, leave again and repeat until all the carbon dioxide has been absorbed by the caustic soda. Finally, remove the caustic soda, level the tube, and read the volume of the gas. Take the temperature of the water and read the barometer.

Next find the volume of the oxygen in the residual gas by means of a piece of yellow phosphorus fastened on a wire. The phosphorus should be left in contact with the gas for several days. Remove the phosphorus, again level, and read the volume of the gas. Take the temperature of the water and read the barometer.

Correct the volumes you have found for temperature and pressure, and calculate the percentage of oxygen, nitrogen, and carbon dioxide in breathed-out air.

Exp. 134—To prepare ammonia and examine its properties

Directions—Mix equal parts of sal ammoniac, NH_4Cl, and slaked lime, and put the mixture into a large boiling tube fitted up in the manner shown in Fig. 86. Heat the mixture strongly, and collect the gas in dry vessels by upward displacement of air. Determine the properties of the gas in the usual way. Also carry out the following experiments :—

(1) Shake up a jar of ammonia with a few drops of copper sulphate solution.

(2) Invert over a jar of ammonia a jar of hydrochloric acid gas. Keep the product.

(3) Carry out the fountain experiment with ammonia.

(4) Make a solution of ammonia in water.

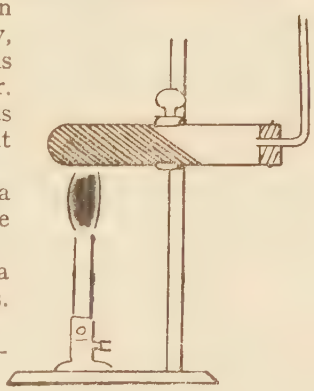


FIG. 86

Exp. 135—To examine some of the reactions of a solution of ammonia in water

Directions—

(1) Boil some of the ammonia solution for ten minutes, and test with copper sulphate solution whether all the ammonia has been driven out of the solution.

(2) To a few c.c. of dilute hydrochloric acid add ammonia solution, stirring continuously, until a drop of the liquid, taken out, is found to have no effect on litmus paper. Carefully evaporate down to dryness. Does the residual white solid resemble ammonium chloride, the solid obtained by mixing gaseous ammonia and gaseous hydrochloric acid? Try the effect of (1) heat, (2) boiling caustic soda solution on the two solids.

(3) Add some ammonia solution to solutions of copper

sulphate, alum, chromium sulphate, ferric chloride, ferrous sulphate, zinc sulphate, and compare the precipitates produced with the hydroxides obtained by adding a solution of caustic soda to solutions of the same substances.

(4) Precipitate some silver chloride, silver bromide, and silver iodide, and try the effect of ammonia solution on the precipitates.

(5) Try the effect of mixing chlorine water and ammonia solution. What is the gas evolved ?

(6) Put some very strong ammonia in a flask placed on a few drops of water on a wooden block, and with the bellows blow a rapid stream of air through the solution. What happens ?

Exp. 136—To examine the effect of heat on ammonium chloride

Directions—(1) Heat some solid ammonium chloride in a dry test-tube. What happens ?

(2) Fit a short asbestos plug into the middle of a wide glass tube about 20 cm. long, and put into the tube ammonium chloride, red and blue litmus paper, and cotton wool in the manner shown in Fig. 87.

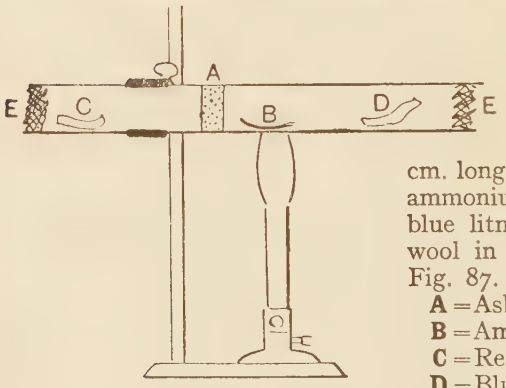


FIG. 87

A = Asbestos.
B = Ammonium chloride.
C = Red litmus paper.
D = Blue litmus paper.
EE = Loose plugs of cotton wool.

Place the tube in a horizontal position and heat the ammonium chloride. Try to explain the colour changes which take place in the litmus papers.

Exp. 137—To test for ammonium

Directions—Carry out the following tests with ammonium salts :—

(1) Heat a solid ammonium salt in an ignition tube. A white sublimate should be formed.

(2) To a solution of an ammonium salt add Nessler's solution (alkaline solution of mercuric iodide in potassium iodide). A yellow coloration or brown precipitate, according to the quantity of ammonium salt, is formed.

(3) Boil with caustic potash solution. Ammonia is given off. Test by smell and with litmus paper.

NITROGEN. Symbol, N

History—Nitrogen was discovered in 1772 by Rutherford. He found that if an animal was placed in a limited quantity of air, and the carbon dioxide produced by its breathing was absorbed with caustic potash, the gas which remained did not support combustion. Lavoisier gave the gas the name *azote* (Greek, *a*, *privative*; *ζωή = life*), to indicate that it would not support life. Chaptal suggested the name nitrogen (Greek, *νίτρον = nitre*; *γεννάω = I produce*), because nitrogen was contained in nitre.

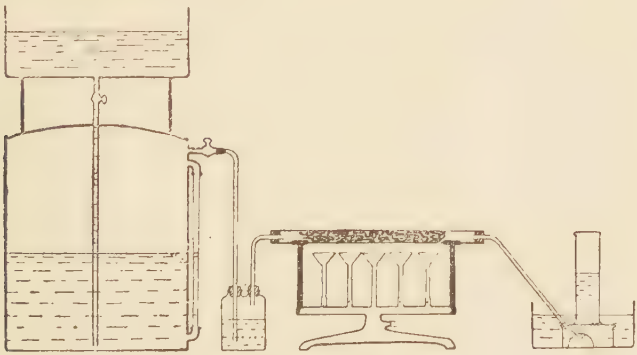


FIG. 88

Occurrence—Nitrogen forms nearly $\frac{4}{5}$ of the air. In combination it is found in nature mainly as saltpetre or nitre, KNO_3, and Chili saltpetre, $NaNO_3$. Lord Rayleigh and Professor Ramsay showed, in 1894, and later, that nitrogen prepared from the air is not pure, but contains about 1 per cent. of argon and its allied elements neon, krypton, and xenon.

Formation—(1) Nitrogen can be obtained by burning phosphorus in air confined under a bell jar over water. The nitrogen obtained contains argon, etc.

(2) Nitrogen can also be obtained by passing air through a wash-bottle containing caustic potash solution to remove carbon dioxide, and then through a long tube containing heated copper. The nitrogen is collected over water. See Fig. 88. The oxygen is taken up by the copper. Nitrogen passes on.

$$2Cu + O_2 = 2CuO$$

(3) Nitrogen can be readily prepared by passing chlorine into excess of a solution of ammonium hydroxide.

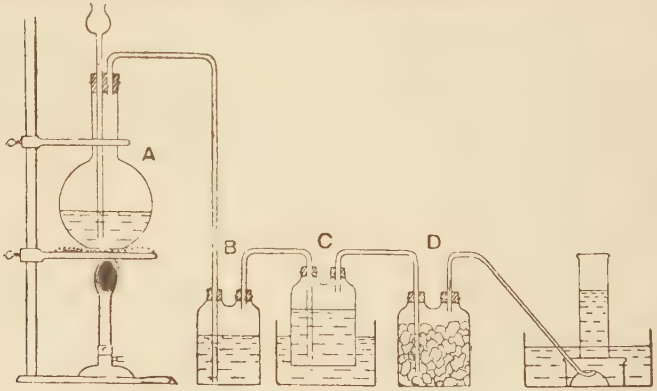


FIG. 89

A is a flask for the generation of chlorine.

B is a bottle containing water to wash the chlorine from HCl.

C is a bottle containing ammonium hydroxide kept cool by cold water.

D is a scrubber containing broken glass or pumice moistened with water to free the nitrogen from fumes of ammonium chloride.

The ammonium hydroxide must be in excess or there is danger of the formation of nitrogen chloride, a very violent explosive.

The ammonia is first decomposed by the chlorine.

$$2NH_3 + 3Cl_2 = N_2 + 6HCl$$

The hydrochloric acid combines with more ammonia to form ammonium chloride.

$$6NH_3 + 6HCl = 6NH_4Cl$$

(4) Nitrogen can be prepared by passing ammonia gas through a long tube containing heated cupric oxide, and collecting over water.

$$3CuO + 2NH_3 = 3Cu + 3H_2O + N_2$$

(5) Nitrogen can be obtained from ammonium chloride by heating it with potassium bichromate. The ammonium chloride is oxidised by the bichromate.

$$K_2Cr_2O_7 + 2NH_4Cl = 2KCl + Cr_2O_3 + 4H_2O + N_2$$

(6) A mixture of ammonium chloride and sodium nitrite, when heated, gives off nitrogen. The salts may be used in the solid state or in strong solution. Ammonium nitrite is formed and is then decomposed.

$$NH_4Cl + NaNO_2 = NH_4NO_2 + NaCl$$
$$NH_4NO_2 = N_2 + 2H_2O$$

The second method of Exp. 131 is the most convenient method for the preparation of nitrogen in the laboratory.

Properties—Density = 14. Atomic weight = 14. Molecular weight = 28. 100 c.c. of water at 0° C. dissolve 2 c.c. of nitrogen. Boiling-point = −195° C.

Nitrogen is a colourless, tasteless, odourless gas, slightly lighter than air. It is almost insoluble in water.

It will not burn or support combustion. Chemically it is very inert. It is difficult to make it combine with anything. It can be made to combine with oxygen by passing sparks from an induction coil through a mixture of nitrogen and oxygen. Red fumes of nitrogen peroxide make their appearance.

It also combines with magnesium and several other metals when they are heated in it.

The absorption of nitrogen by heated magnesium can be demonstrated by means of the apparatus shown in Fig. 90. Magnesium powder is placed in a hard glass tube, fitted with a tube dipping into coloured water and with a short piece of india-rubber tubing fastened with a clip. When the tube is filled with nitrogen and the magnesium is heated, the coloured

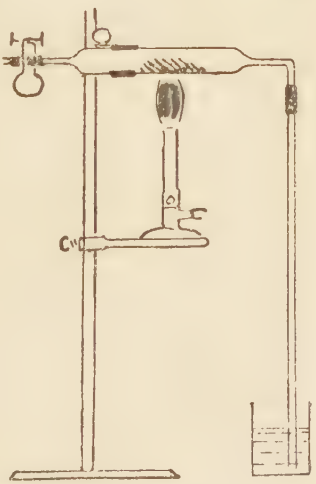


FIG. 90

water is gradually drawn up, owing to the formation of magnesium nitride.

$$N_2 + 3Mg = Mg_3N_2$$

Nitrogen can be condensed under great pressure and at a very low temperature to a colourless liquid, which boils at $-195°$ C.

THE ATMOSPHERE

The atmosphere is the gaseous substance which surrounds the earth. It consists chiefly of nitrogen and oxygen, but contains also argon (and the allied elements neon, krypton, and xenon), carbon dioxide, water vapour, and minute quantities of hydrogen.

Composition of the air by weight

Many analyses of air have been made. In 1841, Dumas and Boussingault determined the parts by weight of nitrogen

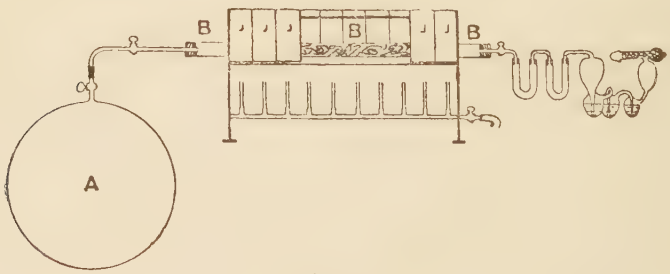


FIG. 91

and oxygen present in air. The chief parts of the apparatus they used are shown diagrammatically in Fig. 91.

A large 10-litre globe **A** was exhausted as completely as possible. Air was freed from carbon dioxide and moisture by passing it through U tubes containing caustic potash and strong sulphuric acid. The air was allowed to enter the globe slowly after passing through a tube **B** containing copper turnings heated to redness. The tube **B** could also be exhausted.

The globe was weighed when vacuous and also after the

experiment. The tube **B** was weighed when vacuous and also after the experiment. At the close of the experiment the tube contained some nitrogen. The weight of the nitrogen was obtained by exhausting the tube and weighing it again. The increase in weight of the globe **A**, plus the weight of the nitrogen in the tube **B**, gave the weight of the nitrogen in the air used. The weight of the oxygen was found from the increase in weight of the tube **B**.

The mean result of numerous experiments was :—

23	parts by weight of	oxygen
77	„	„	nitrogen
100			

Volumetric analysis of air

The most accurate method is the eudiometric method. See Fig. 58. A eudiometer is simply a strong glass tube, accurately graduated, and having two platinum wires sealed through the top.

We know that two volumes of hydrogen unite with one volume of oxygen to form water. The volume of the liquid water produced is so small that it may be neglected. Therefore when a mixture of oxygen and hydrogen is exploded, the contraction is three volumes, or three times the volume of the oxygen present.

To find the volume composition of the air, therefore, air is introduced into a eudiometer and its volume is measured* accurately. More hydrogen than the quantity necessary to combine with the oxygen is next introduced and the volume again accurately measured. The eudiometer is then pressed down tightly on to an india-rubber pad and a spark passed. The volume is again accurately measured. One-third of the contraction observed is equal to the volume of oxygen present. The volume of nitrogen is known from the volume of air and the volume of oxygen.

This method in the hands of a skilled observer will give an accuracy of 1 in 10,000.

* *Measured* in this connection always implies reduction to standard temperature and pressure.

The average composition of air by volume is found to be—

Oxygen	. .	20.96 volumes
Nitrogen, Argon, etc.	. .	79.04 „

Is air a mixture or a compound ?

For a long time air was regarded by chemists as a homogeneous substance. The following considerations point, however, to its being a mixture of nitrogen and oxygen.

(1) Air from different parts of the world varies slightly, but appreciably, in composition. Thus the proportion of oxygen present varies from 20.86 volumes to 20.99 volumes in 100 volumes of air. The composition of a chemical compound cannot vary.

(2) If air is dissolved in water, and the dissolved air is boiled out and analysed, it is found that the dissolved air is richer in oxygen than ordinary air. Oxygen is twice as soluble as nitrogen. If the air is a mixture of oxygen and nitrogen, the oxygen should dissolve in greater proportion than the nitrogen. If, however, air is a compound, air should dissolve as a whole, *i.e.* the dissolved air should have the same composition as ordinary air. Dissolved air has not the same composition as ordinary air. Therefore air is a mixture.

(3) When two substances combine together chemically, heat is generally given out. When oxygen and nitrogen are mixed in the proportions in which they are present in air, no heat is given out, and the mixture has all the properties of ordinary air. Therefore air is a mixture.

(4) Oxygen and nitrogen are not present in air in atomic proportions. Try to obtain a formula for air from the result of the analysis of air by weight.

(5) When liquid air is allowed to boil, nitrogen evaporates more quickly than oxygen. This could not happen if the nitrogen and oxygen were combined.

SUBSTANCES PRESENT IN SMALL QUANTITY IN AIR

Water vapour is present in variable quantity. The higher the temperature, the greater the amount of water vapour that the air can take up. When the temperature of vapour-

saturated air is lowered, the water vapour is precipitated as rain, snow, or hail. More than 140 000 tons of rain would be deposited from a cubic mile of air saturated at 35° and then cooled to 0° C. The air is hardly ever completely saturated, and it hardly ever contains less than one-tenth of the amount of vapour necessary to saturate it.

The amount of moisture in the air may be found by determining the dew-point (see works on Physics), or by slowly drawing a known volume of air through weighed tubes containing calcium chloride or phosphorus pentoxide. The amount of water vapour present in air averages about 1 per cent. per volume.

Carbon dioxide—The amount of carbon dioxide present in air can be determined by drawing a large and measured volume of air, freed from ammonia and water vapour, through tubes containing solid caustic potash. The average of a number of analyses of country air gives the proportion of carbon dioxide as 3 parts in 10,000 parts of air. In the air of towns, where much coal is burnt, the proportions may rise to 6 or 7 parts per 10,000. Air containing more than 7 parts per 10,000 is harmful. In badly ventilated rooms the proportion may rise to 30 parts per 10,000, or even higher. The bad effects produced by breathing such air are probably due more to the organic impurities from the breath than to the carbon dioxide. It is in either case very important to health that the air in rooms should be constantly renewed by good ventilation.

A convenient method for determining the volume of carbon dioxide in the air is that due to Pettenkofer. Fifty c.c. of baryta water are shaken up with about 10 litres of air at a known temperature and pressure. The carbon dioxide precipitates barium carbonate from the solution.

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O$$

Oxalic acid of known strength is then added to the excess of baryta water until it is no longer alkaline. In this way the quantity of baryta water used up by the carbon dioxide may be found, and consequently the weight and volume of carbon dioxide in a given volume of air can be calculated.

Argon, etc.

In 1894 and later, Lord Rayleigh and Professor Ramsay

discovered that if atmospheric air, freed from oxygen, carbon dioxide, water, ammonia, etc., were passed over heated magnesium, the nitrogen could be completely absorbed, but a small quantity of a gas heavier than nitrogen, and with different properties, was left. This gas they called *argon*. Later, it was discovered that the gas they obtained was a mixture of argon with small quantities of other similar gases—neon, krypton, and xenon. The total quantity of these gases present in air is about 1 per cent. Argon and its kindred gases are very inert. Up to the present they have not been made to combine with anything.

Other substances present in air

Ammonia, sulphuretted hydrogen, sulphuric acid, sodium chlorides, oxides of nitrogen, ozone, dust, and smoke occur in small and varying quantities in air. Ammonia is mainly produced by the decay of animal matter. Sulphur compounds are present in the air of towns, owing to the sulphur in the coal burnt. Oxides of nitrogen and ozone are produced during thunderstorms, and probably during the evaporation of sea water especially when large surfaces of wet sand and mud are exposed to the air. The dust and organic impurities are very important, owing to their effect on animals and articles of food. It is owing to the germs present in air that substances ferment and putrefy. Air, filtered from these germs by passage through cotton wool, may be left in contact with milk or the juice of meat for any length of time without production of sourness in the milk or putrefaction in the meat juice. Many diseases are spread among human beings and animals by the germs floating about in the air. The air contains many microbes after a long spell of dry weather, but few after a heavy fall of rain. The raindrops wash the air free from dust and the microbes attached thereto. Over the sea and on high mountains there are few or no microbes in the air. In the country the air contains fewer microbes than in the towns.

It is probable that the dust of dwellings is an important carrier of infection. Cornet found that the dust of inhabited houses contains the consumption bacillus, and that infection with consumption might be produced by means of it. This

dust may be carried in clothing, dirty linen, etc., from the sick and their nurses.

Dust in the air is also a cause of fogs and clouds. In filtered air fog cannot form. The deposit left by a fog consists largely of small particles of carbon. The suspended particles act as nuclei or centres for the deposition of the water forming the fog or cloud.

Height of the atmosphere

The air is elastic and subject to Boyle's Law, and therefore it is less and less dense as the altitude increases. At a height of three and a half miles its density is one-half, at a height of seven miles about one-third of its density at sea level. From observations of the fall of meteors, and of the dust carried round the world by the upper currents of air after the great eruption of Krakatoa, it has been shown that the atmosphere extends to a height of at least 200 miles. It is possible that our atmosphere extends in a rarefied form as far as the moon.

The blue colour of the sky may be due to the scattering of blue light by minute particles of dust present in the air or to the oxygen. Liquid oxygen is blue. Possibly gaseous oxygen, seen in large quantity, is also blue.

AMMONIA, NH_3

History—In solution, and as ammonium salts, it was known to the alchemists. The solution was called *spirits of hartshorn*, owing to the fact that it could be obtained by the destructive distillation of animal refuse, such as horns and hoofs. Priestley first collected the gas over mercury in 1774.

Occurrence—It occurs in small quantities in the air, into which it comes from the decay of nitrogenous matter.

A stable usually smells of ammonia.

Ammonia is found as chloride and sulphate near active volcanoes. The chief source of ammonia is the ammoniacal liquor of the gas works.

Formation—(1) Very small quantities of ammonia can be obtained by subjecting a mixture of nitrogen and hydrogen to the silent discharge in an ozone tube.

$$N_2 + 3H_2 = 2NH_3$$

(2) Ammonia is prepared by heating ammonium salts with caustic potash and soda, or with slaked lime.

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O$$

The gas cannot be dried by means of sulphuric acid or calcium chloride, because it combines with them, giving ammonium sulphate $(NH_4)_2SO_4$, and calcium chloride ammonia, $CaCl_2.8NH_3$, respectively. It is therefore dried by passing it through a cylinder of quicklime, see Fig. 92.

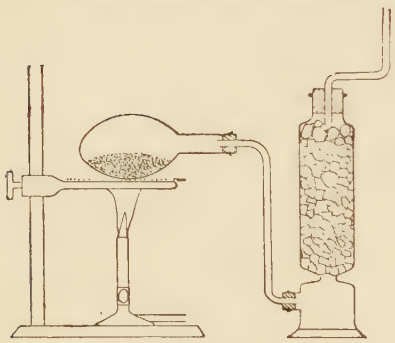


FIG. 92

(3) *Commercial preparation of ammonia from nitrogen. Haber process* Carefully purified nitrogen and hydrogen, in the proportion of one volume of nitrogen to three of hydrogen, are compressed to 200 atmospheres and passed over a mixture of finely divided iron and molybdenum heated to about 500° C. The iron and molybdenum act as a catalyst. The ammonia formed is cooled, and then dissolved in water or liquefied.

Cyanamide process—Nitrogen is passed over calcium carbide heated in an electric furnace. Calcium cyanamide, CN NCa, is produced. The cyanamide is then treated with steam.

$$CN.NCa + 3H_2O = CaCO_3 + 2NH_3$$

This process is used commercially for the preparation of ammonia.

Properties—Density = 8.5. Molecular weight = 17. 1 c.c. of water at 0° C. dissolves 1148 c.c. of ammonia. Melts at −75° C. Boils at −34° C.

Ammonia is a colourless gas with a strong smell and sharp, burning taste. It is lighter than air. It is extremely soluble in water. Its great solubility may be shown by the fountain experiment, see page 175. In this case red litmus is placed in the water of the lower vessel. As soon as the first few drops of water enter the flask filled with ammonia, nearly all

the ammonia is dissolved and he red liquid is forced up as a fountain into the flask, where it is turned blue by the ammonia.

The solution of ammonia is alkaline to litmus, and tastes and smells like the gas. It will readily dissolve silver chloride and, less readily, silver bromide, but it will not dissolve silver iodide. It will precipitate hydroxides of many metals from solutions of their salts, acting in this way like caustic soda.

$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl$$
$$Al_2(SO_4)_3 + 6NH_4OH = 2Al(OH)_3 + 3(NH_4)_2SO_4$$

The solution readily neutralises acids, forming ammonium salts, and water.

$$NH_4OH + HNO_3 = NH_4NO_3 + H_2O$$

Ammonium nitrate

$$2NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O$$

Ammonium sulphate

When a solution of ammonia is boiled, all the dissolved gas is expelled.

If a current of air is blown through a strong solution, the ammonia is quickly carried away as gas. The heat, which is necessary to convert the liquid into a gas (latent heat), must be here drawn from the rest of the solution. The temperature can be lowered in this way to about $-40°$ C. Consequently, if a current of air is blown through a flask containing strong ammonia solution, and placed on a few drops of water poured on a wooden block, the water is quickly converted to ice and the flask firmly frozen to the block.

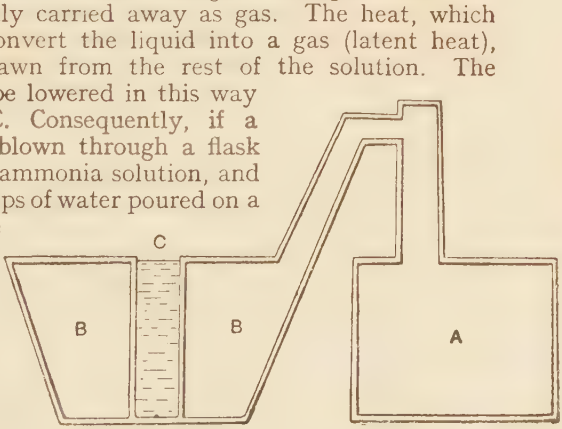


FIG. 93

Ammonia is readily liquefied by pressure. Thus, at ordinary temperatures a pressure of about seven atmospheres converts the gas into a colourless liquid.

Liquid ammonia is made use of in the Carré process for the production of artificial ice. Fig. 93 shows diagrammatically the apparatus used. A very concentrated solution of ammonia is put into a strong iron cylinder **A**, which is connected by strong tubes to the strong vessel **BB**. This surrounds a space **C**, which is filled with water. The solution in **A** is warmed with hot water. Ammonia passes into the vessel **BB**, which is kept cool by water, and is there condensed by its own pressure into liquid ammonia. When **BB** is full of liquid ammonia, **C** is filled with water and **A** is surrounded with cold water. The liquid ammonia in **BB** rapidly evaporates, and the heat which it absorbs is taken mainly from the water in **C**, which is therefore frozen to a cylinder of ice.

Gaseous ammonia will not burn in air under ordinary conditions, nor will it support combustion. If, however, the ammonia be first passed through a strongly heated tube, it will burn in air with a greenish-yellow flame.

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

Ammonia can be made to burn in oxygen by means of the apparatus shown in Fig. 94.

The ammonia solution in the flask is warmed, and the gaseous ammonia escapes from the inner tube. Through the outer tube oxygen from a gas holder is passed. When the oxygen is turned off, the flame of the burning ammonia at once goes out.

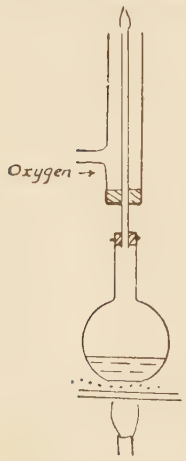


FIG. 94

When a jar of gaseous ammonia is inverted over a jar of hydrochloric acid gas, fumes of ammonium chloride are produced.

$$NH_3 + HCl = NH_4Cl$$

If electric sparks from an induction coil are passed through gaseous ammonia, the gas is completely split up into nitrogen and hydrogen.

$2NH_3$	=	N_2	+	$3H_2$
4 volumes		2 volumes		6 volumes

That ammonia contains only hydrogen and nitrogen is shown by the formation of small quantities of ammonia, when a mixture of nitrogen and hydrogen is subjected to the silent discharge. Chlorine will unite with an

equal volume of hydrogen to form hydrochloric acid. If ammonia is treated with chlorine, the chlorine unites with the hydrogen and sets free nitrogen. Advantage is taken of this fact to find the proportions (by volume) of hydrogen and nitrogen which combine to form ammonia.

A tube about 30 inches long, fitted with a cork and dropping funnel, is filled with chlorine which has been washed free from hydrochloric acid. See Fig. 95. The tube is marked off into three equal divisions by strips of gummed paper. From the funnel, ammonia solution is admitted, a drop at a time. A feeble flash of light is produced with the first few drops. The tube is cooled, one or two c.c. of ammonia solution are run in, and then dilute sulphuric acid, to remove ammonia gas, as long as it will run into the cooled tube. It will be seen that two-thirds of the tube is filled. The gas occupying the other third is found on testing to be nitrogen.

FIG. 95

The three volumes of chlorine must have combined with three volumes of hydrogen derived from the ammonia. The nitrogen which was combined with these three volumes of hydrogen is set free and is found to occupy one volume.

∴ In ammonia 3 volumes of hydrogen are combined with 1 volume of nitrogen.

∴ In ammonia 3 molecules of hydrogen are combined with 1 molecule of nitrogen (Avogadro's Law).

∴ In ammonia 6 atoms of hydrogen are combined with 2 atoms of nitrogen.

∴ The formula of ammonia is $(NH_3)_x$.

The density of ammonia is 8.5. ∴ The molecular weight is 17.

But 1 atom of nitrogen weighs 14, and one atom of hydrogen weighs 1.

∴ $(14+3)_x=17$. ∴ $x=1$. ∴ The formula of ammonia is NH_3.

Tests for ammonia

(1) Ammonia is recognised by its smell, its action with litmus, and the formation of white fumes of ammonium chloride with gaseous hydrochloric acid.

(2) Combined ammonia, as ammonium, may be detected by boiling the substance with caustic soda solution and testing the gas evolved.

$$NH_4Cl + NaOH = NH_3 + NaCl + H_2O$$

(3) Nessler's solution is an alkaline solution of the double salt $HgI_2.2KI$, mercuric iodide combined with potassium iodide. If this solution is added to a solution containing ammonia or an ammonium salt, a brownish coloration or precipitate is produced according to the amount of ammonia present. The test is very delicate.

$$NH_4Cl + 2\{HgI_2.2KI\} + 4KOH = \underset{\text{Brown precipitate}}{NHg_2I.H_2O} + 7KI + KCl + 3H_2O$$

Dissociation of ammonium chloride

The density of the vapour of ammonium chloride, if the formula is NH_4Cl, should be $\frac{14+4+35.5}{2} = \frac{53.5}{2} = 26.75$.

The actual density of the vapour is, however, only 13.375. Now, if ammonium chloride were split up into ammonia and hydrochloric acid on conversion to vapour, the density would be the average density of these two gases.

Density of $NH_3 = \frac{17}{2} = 8.5$. Density of $HCl = \frac{36.5}{2} = 18.25$.

Therefore the average density of a mixture of equal volumes of these gases would be $\frac{8.5+18.25}{2} = 13.375$.

That ammonium chloride does split up, or dissociate, into these two gases on heating, was shown by the experiment with the tube containing a plug of asbestos and the red and blue litmus papers. The blue litmus paper, on the same side of the plug as the sal ammoniac, was turned red, and the red paper on the other side was turned blue. Graham's law of diffusion of gases states that the rate of diffusion of a gas is inversely as the square root of its density. The ammonia, therefore, will diffuse through the asbestos plug faster than the hydrochloric acid, producing excess of ammonia beyond the plug, and leaving excess of hydrochloric acid on the ammonium chloride side of the plug. The result of the experiment bears out this explanation.

We may conclude, therefore, from this experiment and from the density of ammonium chloride vapour, that ammonium chloride, when vaporised, splits up completely into ammonia and hydrochloric acid.

$$NH_4Cl = NH_3 + HCl$$

PRACTICAL EXERCISES

(1) Determine the weights of carbon dioxide and water vapour in 10 litres of air at the temperature of the laboratory.

(2) Find the weight of NH_3 in 1 c.c. of the given strong ammonia solution. Standard acid is provided.

(3) Pass ammonia over copper oxide heated to redness in a hard glass tube. Collect and identify the products.

CHAPTER XXI

OXIDES AND OXYACIDS OF NITROGEN

Exp. 138—To observe the difference of behaviour of ammonium chloride and ammonium nitrate when these salts are heated

Directions—Heat the two salts in test-tubes and test the gases evolved. Notice all the changes that take place.

Exp. 139—To prepare nitrous oxide and investigate its properties

Directions—Into a small dry flask put a few grams of ammonium nitrate ; heat gently and collect the gas evolved over water. As the gas is somewhat soluble in cold water, it should, if possible, be collected over warm water.

Caution—Do not heat the ammonium nitrate strongly, or an explosion may occur.

Test the gas in the usual way. Try also the effect of introducing into the gas sulphur burning feebly and also sulphur burning vigorously. Do the same with phosphorus.

Exp. 140—To prepare nitric oxide and investigate its properties

Directions—Into a flask, fitted with a thistle funnel and delivery tube, put some copper turnings. Cover the turnings with water and then pour strong nitric acid down the funnel until the gas comes off briskly. Collect over water.

Test the gas in the usual way.

Also try its action with feebly and brightly burning sulphur and phosphorus.

Into the gas, contained in a jar inverted in water, pass oxygen, a few c.c. at a time. What happens? Test the water in the jar with litmus.

Into another jar of the gas put a few drops of carbon bisulphide, shake well with a glass plate on the top of the jar, and apply a light.

Exp. 141—To prepare nitrogen peroxide and investigate its properties

Directions—Fit a hard glass tube with a cork and a delivery tube. Heat some powdered lead nitrate in the hard glass tube. Collect a jar or two of the heavy brown gas by downward displacement of air, and test the gas in the usual way.

Next fit a U tube on to the delivery tube, surround the U tube with a freezing mixture, and collect as much liquid nitrogen peroxide as you can.

(1) Note the change of colour of the liquid as the temperature rises.

(2) Put a few drops of the liquid into a small flask and warm until no liquid remains. Then heat the flask in the bunsen flame fairly strongly. Allow it to cool. Note the change of colour of the gaseous nitrogen peroxide with change of temperature.

(3) Add a few drops of the liquid to water. Test a portion of the solution with litmus. Next add strong sulphuric acid to the remainder, cool, and finally pour ferrous sulphate solution very carefully down the side of the tube. You should obtain a brown ring where the liquids meet.

Exp. 142—To prepare a solution of nitrous acid and investigate its properties

Directions—Dissolve a few grams of potassium nitrite in water, cool well, and then slowly add dilute sulphuric acid. Test portions of the solution as follows:—

(1) Add indigo solution.

(2) Add potassium iodide solution and afterwards starch solution.

(3) Add a few drops of acidified potassium permanganate solution.

(4) Pass sulphuretted hydrogen through the solution.

(5) Add ferrous sulphate solution. Warm the mixture and test for a ferric salt. (See Appendix.)

Is nitrous acid an oxidising or a reducing agent ?

Exp. 143—To prepare nitric acid and investigate its properties

Directions—Into a retort, connected to a flask cooled by water, put some sodium nitrate or potassium nitrate and cover the salt with strong sulphuric acid. Gently heat the mixture. Try the following tests with the nitric acid which distils over :—

(1) Warm a few drops with indigo solution.

(2) Add potassium iodide solution and afterwards starch solution.

(3) Try the effect of nitric acid on small pieces of cloth.

(4) Heat some fine sawdust until it begins to char, and then pour a few drops of nitric acid on it.

(5) Try the effect of hot and cold nitric acid of various strengths on the metals—iron, copper, tin, lead, magnesium, zinc.

Exp. 144—To compare the properties of nitrites and nitrates

Directions—(1) Warm each with dilute sulphuric acid.

(2) Try the effect of strong sulphuric acid on each.

(3) Heat each strongly, notice any changes, and test for oxygen.

(4) To a solution of each add dilute sulphuric acid, potassium iodide solution, and starch solution.

(5) To a cold solution of each add *dilute* sulphuric acid and then ferrous sulphate solution.

Make a table of your results.

NITROUS OXIDE (*Laughing Gas*), N_2O

History—The gas was discovered by Priestley in 1772.

Formation—It is obtained by heating ammonium nitrate in a flask fitted with a cork and delivery tube. The gas is collected over hot water.

$$NH_4NO_3 = N_2O + 2H_2O$$

If the salt is heated strongly the decomposition becomes violent and even explosive, and some nitric oxide is formed.

Properties—Molecular weight = 44. Density = 22. 1 c.c. of water at 10° C. dissolves about 1 c.c. of gas. Melts at −99° C. Boils at −92° C.

Nitrous oxide is a colourless gas with a faint, rather pleasant smell and a sweet taste. It dissolves in about its own volume of water. Its solution does not affect litmus.

It will not burn, but will support combustion. It will relight a glowing splinter. If feebly burning sulphur is put into the gas the flame is extinguished, but if the sulphur is burning brightly it goes on burning with increased brilliancy. The feebly burning sulphur is not hot enough to split up the gas, whereas the brightly burning sulphur is hot enough to decompose it into nitrogen and oxygen. In the oxygen thus set free, the sulphur burns with increased brilliancy, because the oxygen is present in a proportion greater than in air.

$$S + 2N_2O = SO_2 + 2N_2$$

Nitrous oxide may be distinguished from oxygen by putting nitric oxide into a jar of the gas inverted in water. With oxygen, nitric oxide forms brown fumes of nitrogen peroxide ; with nitrous oxide, nitric oxide has no reaction.

When mixed with air and inhaled, nitrous oxide produces excitement which often takes the form of hysterical laughter ; hence the name *laughing gas*. If the pure gas is inhaled for a short time it produces insensibility ; it leaves no bad after-effects, and therefore it is much used by dentists. For dental purposes the gas should be purified from traces of nitric oxide and chlorine by passing it through ferrous sulphate solution and caustic soda solution respectively.

When inhaled for a longer period it causes death.

It can be condensed fairly easily, becoming a colourless, mobile liquid.

Composition—Some nitrous oxide is collected over mercury in a bent tube. See Fig. 96. A piece of potassium is introduced and shaken to the upper end of the tube. The potassium is then gently heated. It burns in the gas, forming potassium oxide, and setting free nitrogen. The nitrogen is found to occupy the same volume as the nitrous oxide.

∴ 1 volume of nitrous oxide contains 1 volume of nitrogen.

∴ 1 molecule of nitrous oxide contains 1 molecule of nitrogen.

∴ The formula of the gas is N_2O, N_2O_2, N_2O_x.

The density of nitrous oxide is 22.

∴ The molecular weight = 44.

But two atoms of nitrogen weigh 28.

∴ A molecule of nitrous oxide contains 44 − 28 = 16 parts of oxygen, *i.e.* one atom of oxygen.

∴ The formula of nitrous oxide is N_2O.

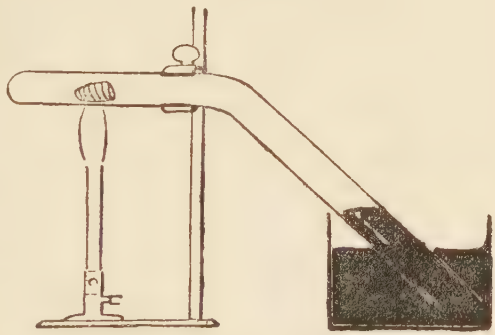


FIG. 96

NITRIC OXIDE, NO

History—Nitric oxide was obtained by Van Helmont, but first investigated by Priestley.

Formation—(1) Nitric oxide is prepared by treating copper with nitric acid, diluted with its own volume of water. The gas is collected over water.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$

Prepared in this way the gas usually contains traces of nitrous oxide and sometimes of nitrogen. These impurities rapidly increase in quantity as the amount of copper nitrate in solution increases and as the temperature rises.

(2) Pure nitric oxide is obtained by warming with strong sulphuric acid a mixture of 1 part of nitre, 4 parts of ferrous sulphate, and a few c.c. of water.

$$2KNO_3 + 6FeSO_4 + 5H_2SO_4 = 2KHSO_4 + 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

Properties—Density = 15. Molecular weight = 30. Almost insoluble in water. Boils −153.6° C.

Nitric oxide is a colourless gas which is almost insoluble in water. Its smell cannot be determined, as it forms brown

fumes of nitrogen peroxide as soon as it comes into contact with the oxygen of the air.

$$2NO + O_2 = 2NO_2$$

This property readily distinguishes it from *all* other gases.

It will not burn nor relight a glowing splinter. Nitric oxide is the most stable of the oxides of nitrogen. It is not split up at a low red heat. Burning sulphur is extinguished by the gas, but phosphorus, when burning brightly, splits up the gas into nitrogen and oxygen, and burns with increased brightness in the oxygen set free.

$$4P + 10NO = P_4O_{10} + 5N_2$$

If a few drops of carbon bisulphide are shaken up in a jar of nitric oxide, and a light is applied to the jar, the mixture of nitric oxide and carbon bisulphide vapour burns with a brilliant bluish flame. This flash is very rich in acitinic rays, the rays which affect a photographic plate. It can therefore be used as a flash-light for photographing dark interiors.

Nitric oxide dissolves in a solution of ferrous sulphate, producing a dark brown solution which contains the unstable compound $2FeSO_4.NO$. If the solution is warmed, the compound is split up and pure nitric oxide is given off. Nitric oxide could therefore readily be purified or separated from other gases by means of ferrous sulphate solution.

Composition—If potassium is heated in nitric oxide contained in a bent tube over mercury, it takes out oxygen from the nitric oxide and leaves a volume of nitrogen equal to half the volume of the nitric oxide used. See Fig. 96.

∴ 1 volume of nitric oxide contains $\frac{1}{2}$ a volume of nitrogen.

∴ 1 molecule of nitric oxide contains $\frac{1}{2}$ a molecule of nitrogen.

∴ 1 molecule of nitric oxide contains 1 atom of nitrogen.

∴ The formula of the compound is NO, NO_2, or NO_x.

The density of nitric oxide is 15.

∴ Its molecular weight is 30.

∴ A molecule of nitric oxide contains $30 - 14 = 16$ parts of oxygen, or 1 atom of oxygen.

∴ The formula for nitric oxide is NO.

NITROGEN TRIOXIDE, N_4O_6

When arsenious oxide (white arsenic), As_4O_6, is warmed

with strong nitric acid, a red gas is produced which may be condensed to a blue liquid by means of a freezing mixture.

$$As_4O_6 + 4HNO_3 + 4H_2O = N_4O_6 + 4H_3AsO_4$$

Arsenic acid

At $-9°$ C. nitrogen trioxide is a blue liquid, but the colour changes to green as the temperature rises. It dissolves in ice-cold water, forming nitrous acid. $N_4O_6 + 2H_2O = 4HNO_2$.

When the liquid N_4O_6 is allowed to evaporate, a mixture of nitric oxide and nitrogen peroxide is evolved.

$$N_4O_6 = 2NO_2 + 2NO$$

H. B. Baker and Mrs. Baker have recently shown, however, that nitrogen trioxide exists in the gaseous state in absence of moisture as N_4O_6.

NITROGEN PEROXIDE, NO_2 and N_2O_4

Formation—(1) Nitrogen peroxide is prepared by heating lead nitrate, and condensing the gas evolved in a U tube immersed in a freezing mixture.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

(2) It is also obtained by mixing one volume of oxygen with two volumes of nitric oxide, and passing the mixture through a tube cooled in a freezing mixture.

$$2NO + O_2 = 2NO_2$$

Properties—Molecular weight = 46 and 92. Density = 23 and 46. Melts at $-9°$ C. Boils at 22° C.

Nitrogen peroxide is a colourless, crystalline compound which melts at $-9°$ C. to a pale yellow liquid. This liquid deepens in colour to orange at ordinary temperatures and boils at 22° C., giving a reddish brown vapour. The vapour, just above the boiling-point, has a density of about 46, a density corresponding to the formula N_2O_4. As the temperature is raised, the colour gets deeper and the density gets smaller, until at 140° C. the colour is almost black and the density is 23, a density corresponding to the formula NO_2. At 600° the colour again fades, owing to the splitting up of nitrogen peroxide into nitric oxide and oxygen.

$$2NO_2 = 2NO + O_2$$

When the gas is cooled again, the changes take place in the reverse order.

When treated with a small quantity of cold water, nitrogen peroxide forms a mixture of nitric and nitrous acids.

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

With excess of water at the ordinary temperature, it forms nitric acid and nitric oxide.

$$3NO_2 + H_2O = 2HNO_3 + NO$$

Gaseous nitrogen peroxide, like nitric oxide, will only support the combustion of substances which burn at a temperature sufficiently high to split up the gas.

NITROGEN PENTOXIDE (*Nitric anhydride*), N_2O_5

Formation—(1) When the strongest nitric acid is cautiously added to phosphorus pentoxide in the proportions indicated in the equation below, and the mixture is gently heated, nitrogen pentoxide distils over. The pentoxide is collected in a well-cooled receiver.

$$4HNO_3 + P_4O_{10} = 2N_2O_5 + 4HPO_3$$

Metaphosphoric acid

(2) It can also be made by passing dry chlorine over dry silver nitrate.

$$4AgNO_3 + 2Cl_2 = 2N_2O_5 + 4AgCl + O_2$$

Properties—Nitric anhydride is a white, crystalline solid which melts at 30° C. If heated further it decomposes, giving off dense brown fumes of nitrogen peroxide. When heated suddenly it explodes, giving nitrogen peroxide and oxygen. Explosion may take place at ordinary temperatures if the oxide has been kept for some time. It is a powerful oxidiser.

It dissolves in water with evolution of much heat and forms nitric acid. Hence the name nitric anhydride.

$$N_2O_5 + H_2O = 2\ HNO_3$$

NITROUS ACID (HNO_2) AND NITRITES

Nitrous acid solution can be obtained by dissolving nitrogen trioxide in cold water, or by acidifying a nitrite with dilute acid.

$$N_2O_3 + H_2O = 2HNO_2$$
$$NaNO_2 + HCl = NaCl + HNO_2$$

The acid is not known in the pure state. Even the aqueous solution rapidly decomposes.

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

The solution sometimes acts as a reducing agent. It will decolorise acidified potassium permanganate solution, and change yellow potassium chromate (acidified) into green

chromium salt. This is owing to the ease with which it is oxidised to nitric acid. $2HNO_2 + O_2 = 2HNO_3$.

More frequently it acts as an oxidising agent. Thus, it sets free iodine from an acidified potassium iodide solution and sulphur from sulphuretted hydrogen.

$$2HNO_2 + 2KI + 2HCl = 2KCl + I_2 + 2NO + 2H_2O$$
$$2HNO_2 + H_2S = S + 2H_2O + 2NO$$

The nitrites are stable compounds. Those of potassium and sodium may be obtained by heating the nitrates of these metals. $2KNO_3 = 2KNO_2 + O_2$.

Other nitrites may be formed by passing nitrogen trioxide into solutions of the bases.

Nitrites give off oxides of nitrogen when treated with dilute acids, and, when acidified, they turn out odine from potassium iodide solution. Nitrates do not react in this way. When acidified with dilute acids, nitrites give a brown coloration with ferrous sulphate solution. Nitrates do not do this.

NITRIC ACID, NHO_3

History—Nitric acid (aqua fortis) was well known to the alchemists. Lavoisier first showed that it contained oxygen. Cavendish was the first to synthesise it. He obtained it by sparking nitrogen and oxygen in the presence of water.

Formation—(1) Nitric acid is prepared in the laboratory by heating saltpetre in a retort with an equal weight of strong sulphuric acid, and condensing the nitric acid in a well-cooled receiver. See Fig. 97.

$$KNO_3 + H_2SO_4 = HNO_3 + KHSO_4$$
Potassium hydrogen sulphate

The acid obtained contains some water. Its yellow colour is due to dissolved oxides of nitrogen. It may be freed from water by distillation with an equal volume of strong sulphuric acid. The oxides of nitrogen may be removed from the distillate by warming it gently and passing a current of dry air through it until it is cold.

(2) Nitric acid can be obtained by passing sparks through a mixture of nitrogen and oxygen in presence of a small quantity of water. The red fumes of the nitrogen peroxide produced dissolve in the water, forming nitric acid and nitric oxide.

$$3NO_2 + H_2O = 2HNO_3 + NO$$

(3) Nitric acid is manufactured from Chili saltpetre, $NaNO_3$, by distilling the salt with sulphuric acid from iron retorts and collecting the nitric acid in stoneware bottles.

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3$$

The temperature used is sufficiently high to cause the conversion of the sulphuric acid to the normal sulphate.

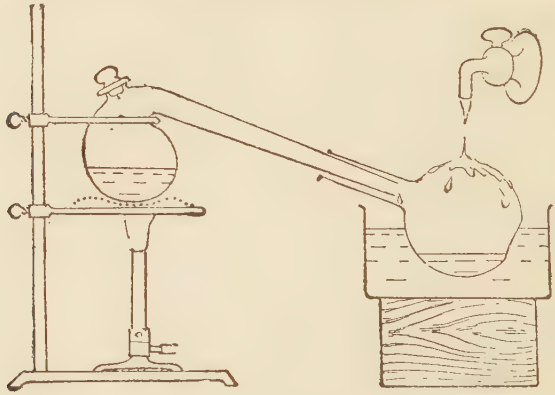


FIG. 97

(4) *Manufacture of nitric acid from the nitrogen of the air.*

(*a*) *Direct combination of nitrogen and oxygen*—

Air is passed through an electric arc. A small percentage of the nitrogen and oxygen combine to form nitric oxide, NO. The hot gases from the arc are made to give up part of their heat to fresh air entering the arc, and most of their remaining heat to pipes passing through a boiler. The steam generated is used to concentrate the solutions of nitrates obtained later. When the temperature of the nitric oxide is reduced below 600° C., the gas combines with the oxygen of the excess air to form nitrogen peroxide, NO_2.

The gases next pass up towers down which water is sprayed. Nitric acid and nitric oxide are obtained as in method (2) above; the nitric oxide combines with more oxygen from the excess air, and practically all the nitric oxide is in this way converted into a weak solution of nitric acid. This weak nitric acid solution can be concentrated to about 35 per cent. by spraying it again and again down the towers in place of the water.

The nitric acid solution is usually neutralised by lime, and the solution evaporated until calcium nitrate is obtained as a white solid. The calcium nitrate is used as an artificial manure or "fertiliser."

(*b*) *Oxidation of ammonia by air*—

The carefully purified air and ammonia (see p. 244) are passed through platinum gauze at a temperature of 500–600° C. When once started the action proceeds automatically, since the chemical reaction is *exothermic* and enough heat is produced to maintain the platinum at the required temperature.

The reactions are—

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$
$$2NO + O_2 = 2NO_2$$

The nitrogen peroxide is converted into nitric acid or calcium nitrate as in (*a*).

Properties—Density abnormal. Molecular weight=63. Boils at 86° C. Mixes with water in all proportions.

Pure nitric acid is a colourless, fuming liquid. Its specific gravity is about 1.5. It has a peculiar choking smell. It fumes strongly in the air, owing to absorption of atmospheric moisture. It stains the skin and other organic materials yellow, and causes painful wounds when allowed to remain in contact with the flesh. It oxidises fine dry sawdust sufficiently rapidly to cause it to light.

Weak nitric acid, if boiled, loses water and becomes stronger; strong nitric acid, if boiled, partly breaks up into water, nitrogen peroxide, and oxygen, and becomes weaker; in both cases an acid, distilling unchanged at 120° C., and containing about 68 per cent. of HNO_3, is finally obtained. The composition of the distillate is found to vary with the pressure; it is therefore not a chemical compound of nitric acid and water.

The vapour density of nitric acid is abnormal. The acid is partly split up at the boiling-point into a mixture of nitrogen peroxide, water, and oxygen.

Nitric acid is a very powerful oxidising agent. Sulphur is transformed by it into sulphuric acid, phosphorus into phosphoric acid, carbon to carbon dioxide, and tin to a hydrated oxide, called metastannic acid, $5SnO_2.5H_2O$. Oxides of nitrogen are given off in each case in proportions varying with the conditions, so that the changes cannot well be expressed by equations.

Hydrogen is not evolved, as a rule, when nitric acid is treated with metals. The nitric acid is reduced to oxides of nitrogen, nitrogen, or even to ammonia. Alteration of temperature, dilution of the acid, and the presence of salts in solution, all have their effect on the gaseous products of the reaction. Three of the more important actions are represented by the following equations :—

Dilute and cold acid
$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$
$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 5H_2O + N_2O$$

Hot and strong acid
$$5Sn + 20HNO_3 = \underset{\text{Metastannic acid}}{H_{10}Sn_5O_{15}} + 20NO_2 + 5H_2O$$

For a fuller account of the action of nitric acid on the metals see page 343.

Most metals are attacked by nitric acid. Gold and platinum are unattacked by it, but they are soluble in aqua regia, which is a mixture of one part of nitric acid with about three parts of strong hydrochloric acid. The solvent action of this mixture is due to the nascent chlorine set free by the oxidation of the hydrochloric acid by the nitric acid. Thus—

$$HNO_3 + 3HCl = 2H_2O + Cl_2 + \underset{\text{Nitrosyl chloride}}{NOCl}$$

Nitric acid is a monobasic acid. It neutralises bases forming nitrates.

$$Ca(OH)_2 + 2HNO_3 = Ca(NO_3)_2 + 2H_2O$$
$$NaOH + HNO_3 = NaNO_3 + H_2O$$

Nitric acid is very useful for replacing a hydrogen atom in organic compounds by an NO_2 group. Thus nitrobenzene is made by treating benzene with a mixture of strong nitric acid and strong sulphuric acid. The sulphuric acid is present to absorb the water produced.

$$\underset{\text{Benzene}}{C_6H_6} + HNO_3 = \underset{\text{Nitrobenzene}}{C_6H_5.NO_2} + H_2O$$

Again, the explosives, gun-cotton and nitroglycerine, are made by treating cotton wool and glycerine respectively with a mixture of nitric and sulphuric acids. Gun-cotton is hexa-nitro-cellulose, $C_{12}H_{14}(NO_2)_6O_{10}$, and nitroglycerine is glyceryl-tri-nitrate, $C_3H_5(NO_3)_3$.

Nitrates

When nitrogenous matter undergoes slow oxidation in the

air in presence of water and a base, a nitrate of the base is formed. In this way are formed the nitrates in the soil which are so important to the life of plants. In Chili, Peru, and India, in hot and rainless districts, nitrates of sodium and potassium are sometimes found as a crystalline efflorescence on the soil. Why are they found only in rainless districts ?

All nitrates of metals are soluble in water. They are good oxidising agents. If nitre, KNO_3, is melted, and small pieces of charcoal are added to it, the carbon is rapidly burnt away to carbon dioxide. It is the nitre in gunpowder that provides the oxygen for the burning of the other constituents, sulphur and charcoal.

When nitrates of monad metals, such as potassium and sodium, are heated, nitrites are formed and oxygen is given off.

$$2KNO_3 = 2KNO_2 + O_2$$

Nitrates of diad metals, such as lead and copper, break up when heated into the oxide of the metal, nitrogen peroxide, and oxygen.

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

Ammonium nitrate decomposes on heating into water and nitrous oxide.

$$NH_4NO_3 = N_2O + 2H_2O$$

It is used as a constituent of several modern explosives.

Nitrates may readily be distinguished from nitrites by the fact that they do not, like nitrites, give off red fumes of oxides of nitrogen when warmed with dilute acids, and also by the fact that they do not give a brown coloration with ferrous sulphate solution which has been acidified with dilute acids.

If, however, nitrates are mixed with strong sulphuric acid, and a solution of ferrous sulphate is carefully poured down the side of the tube, a brown ring of $2FeSO_4.NO$ is formed at the plane where the liquids meet.

PRACTICAL EXERCISES

(1) Find the weight of a litre of nitric oxide.

(2) Determine the purity of commercial strong nitric acid. Standard caustic soda is provided.

(3) From copper oxide prepare a dry crystalline specimen of copper nitrate. Determine the percentage of copper oxide in your specimen.

CHAPTER XXII

PHOSPHORUS AND ITS COMPOUNDS

Exp. 145—To compare the properties of red and yellow phosphorus

Directions—Yellow phosphorus must not be touched with the fingers unless it is under water.

Carry out the following experiments *with very small quantities* of each substance :—

(1) Note the colour, texture, hardness, and general appearance.

(2) Place in a test-tube, add water, put a thermometer in the tube, and gently warm the tube in the water bath. Note the melting-point of the phosphorus. Repeat the experiment.

(3) Warm with a few c.c. of carbon bisulphide on the water bath, pour the liquid over a filter paper, and allow the paper to stand until it is dry. Explain the result.

Caution—The liquid must on no account be brought near a flame or allowed to touch your hands or clothes.

(4) Place in copper sulphate solution, and allow to stand for some days. Explain the result.

(5) Heat in a hard glass tube.

Tabulate your results for the two forms of phosphorus.

Exp. 146—To examine phosphoric anhydride

Directions—(1) Describe the substance.

(2) Expose a very small quantity to the air for some time and note the changes.

(3) Dissolve about a gram of oxide in water, and nearly neutralise with caustic soda. Add silver nitrate solution.

(4) Dissolve about a gram of oxide in water, boil for some minutes, and then neutralise with caustic soda. Add silver nitrate solution. Contrast the result with that obtained in (3).

(5) Test the pentoxide for the presence of lower oxides of phosphorus by boiling with mercuric chloride solution, which is reduced to white insoluble mercurous chloride by the lower oxides, but is not affected by the pentoxide.

Exp. 147—To prepare and examine phosphoric acid

Directions—(1) Warm about a gram of red phosphorus,

moistened with water, with a few c.c. of strong nitric acid. Use a fairly large flask and take away the flame as soon as the action starts. Evaporate the clear liquid to dryness in an evaporating dish, dissolve the residue in water, and boil the solution obtained.

(2) Test the solution for phosphoric acid by adding strong nitric acid and ammonium molybdate solution and warming. A fine yellow precipitate indicates the presence of phosphoric acid.

(3) Neutralise a portion of the solution, and test with silver nitrate solution.

(4) Warm the solution with mercuric chloride solution. There should be no reduction to mercurous chloride.

(5) Heat some phosphoric acid to redness. Note the characters of the metaphosphoric acid obtained.

(6) Dissolve the metaphosphoric acid in *cold* water and try the effect of the solution on white of egg. Try and compare the action of ordinary phosphoric acid on white of egg.

(7) Neutralise some solution of metaphosphoric acid with ammonia and add silver nitrate solution. Compare the result with that obtained in (3) of the preceding experiment.

Exp. 148—To prepare and examine phosphorous acid solution

Directions—Make a solution of phosphorous acid by adding a few drops of phosphorus trichloride to *cold* water. Test the solution as follows :—

(1) Warm with mercuric chloride solution.

(2) Warm with ammoniacal silver nitrate solution.

(3) Evaporate some solution to dryness. Note, and, if possible, explain what happens. Test the residue for phosphoric acid.

PHOSPHORUS. Symbol, P

History—Brand, a Hamburg alchemist, first obtained phosphorus. He prepared it by evaporating urine to a syrup and distilling the syrup with sand. It remained, however, for Scheele, in 1771, to find out a method of obtaining phosphorus from bone ash.

Occurrence—Phosphorus is never found free. It occurs as the mineral apatite, $3Ca_3(PO_4)_2.CaCl_2$, and in all fertile soils as calcium phosphate, $Ca_3(PO_4)_2$. Phosphates are necessary for plant life. From the plants, phosphorus passes into

animals. Bones contain over 60 per cent., and the ash from bones sometimes contains 90 per cent. of calcium phosphate.

Manufacture—Phosphorus is obtained mainly from bone ash. The finely powdered bone ash is treated in large wooden vessels with fairly strong sulphuric acid, and high pressure steam is driven into the mixture.

$$\underset{\text{Calcium phosphate}}{Ca_3(PO_4)_2} + 3H_2SO_4 = 3CaSO_4 + \underset{\text{Phosphoric acid}}{2H_3PO_4}$$

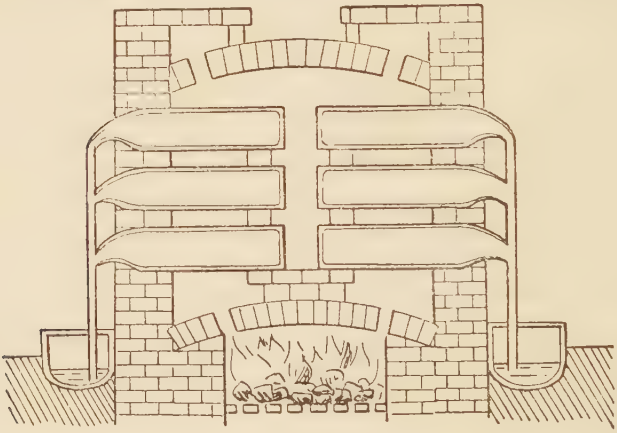


FIG. 98

The product is filtered through a bed of cinders to remove calcium sulphate, and the phosphoric acid solution is concentrated to a syrup in lead-lined pans heated by steam coils.

It is next mixed with sawdust or coarsely ground charcoal. The mixture is dried by heating in a cast-iron pot. The orthophosphoric acid is thus converted into metaphosphoric acid.

$$H_3PO_4 = \underset{\text{Metaphosphoric acid}}{HPO_3} + H_2O$$

Finally the charred product is distilled from bottle-shaped clay retorts heated to whiteness in a furnace. See Fig. 98.

$$4HPO_3 + 12C = P_4 + 2H_2 + 12CO$$

The phosphorus distils into water down iron pipes, which are luted into the retorts. The molten phosphorus is forced through chamois leather and canvas to filter it. It is then cast into sticks.

This process has now been largely displaced by a process of direct formation of phosphorus from calcium phosphate by means of the electric furnace. An intimate mixture of phosphate, carbon, and a flux is distilled from a tightly covered electric furnace from which a pipe leads to a condenser. The phosphorus distils over and is condensed. The residue fuses and is drawn off at intervals as a slag. The following reaction has been suggested for the change :—

$$2Ca_3(PO_4)_2 + 28C = 6CaC_2 + P_4 + 16CO$$

Calcium carbide

Properties of yellow phosphorus—Atomic weight = 31. Vapour density = 62. Molecular weight = 124.

Ordinary phosphorus is a white, translucent, wax-like solid. When exposed to light it becomes yellow, then brown, and finally almost black. At 0° C. it is brittle, at 15° C. it is soft enough to be cut with a knife. It melts under water at 43° C., and in the air at 30° C. It takes fire in the air at 34° C. and burns brilliantly, forming phosphorus pentoxide.

Phosphorus is somewhat volatile at ordinary temperatures. If yellow phosphorus be warmed to about 40° C. in a tube which has been exhausted and sealed, crystals of phosphorus are slowly formed in the cold part of the tube by sublimation.

Yellow phosphorus is insoluble in water, but readily soluble in carbon bisulphide, and to a small extent in oils and in liquid hydrocarbons. If a solution of phosphorus in carbon bisulphide is poured over filter paper and the carbon bisulphide allowed to evaporate, phosphorus is left on the paper in such a finely divided state that it takes fire, owing to rapid oxidation by the air.

Phosphorus is phosphorescent in the dark. Poisonous white fumes of phosphorous oxide, P_4O_6, are given off. The phosphorescence is due to oxidation, for phosphorus will not glow in gases such as nitrogen ; if free oxygen is introduced into the nitrogen the phosphorescence appears. Curiously enough, phosphorus will not glow in pure oxygen. If, however, the oxygen is rarefied by means of an air pump, the phosphorus once more glows. The glowing of phosphorus is supposed to be connected with the formation of ozone, for a stick of phosphorus will not glow in air containing traces of ethylene,

turpentine, or ether—substances which absorb or destroy ozone.

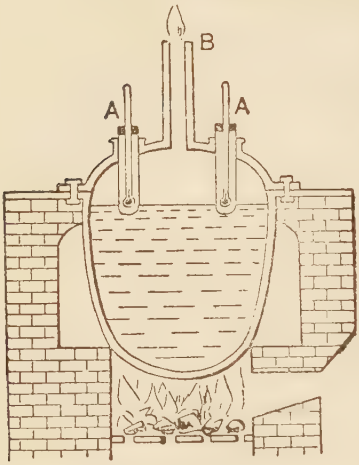


FIG. 99

Phosphorus is very poisonous. Workers in match factories, when yellow phosphorus was used, were liable to develop diseases of the bones of the jaw and nose, owing to their constant exposure to the fumes from the phosphorus. The presence of uncombined yellow phosphorus in a substance may be detected by boiling the substance with water in a flask fitted with a cork and glass jet. The phosphorus vapour, which comes off with the steam, is oxidised by the air. If the flask is heated in a dark room, a dull glow, like a pale flame, can be seen at the jet.

Manufacture of red phosphorus from yellow phosphorus

Red phosphorus is made on the large scale by heating yellow phosphorus to about 240° C. in a cast-iron pot. Fig. 99. This pot is provided with metal tubes, **AA**, containing thermometers, and with a short open tube **B**. The tube **B** acts as a safety valve. If the temperature rose above 260°, the red phosphorus would be converted into yellow phosphorus, with evolution of so much heat that a completely closed vessel would probably burst.

The small quantity of unchanged yellow phosphorus is removed from the powdered red phosphorus by boiling with caustic soda solution. The red phosphorus is then washed and dried.

Properties—Red phosphorus is a chocolate-red powder, which has the specific gravity 2.2. It has neither taste nor smell. It is not poisonous, and it is insoluble in carbon bisulphide. It is not oxidised by dry air at ordinary temperatures. It is not luminous in the dark. Heated in air, it ignites at about 240° C.

Red phosphorus is often called amorphous phosphorus.

This is not a correct name, for red phosphorus under the microscope appears to be crystalline.

Schenk's scarlet phosphorus is a third form of phosphorus. It is obtained as a precipitate when a solution of yellow phosphorus in phosphorus tribromide, PBr_3, is boiled. It is non-poisonous, does not oxidise in air, and is more active than red phosphorus.

Matches—Phosphorus is chiefly used for the manufacture of matches. Friction matches are generally made by dipping wooden splints into melted paraffin wax and then into a paste of Schenk's scarlet phosphorus, potassium chlorate, red lead and glue. The potassium chlorate provides oxygen for the ignition of the phosphorus. Many makers replace potassium chlorate with potassium nitrate, as matches made with the latter are less liable to ignite explosively when rubbed on a rough surface.

Safety matches have largely replaced friction matches. The heads of these matches consist of a mixture of potassium chlorate, potassium bichromate, red lead, and antimony sulphide. They are ignited by rubbing on a surface coated with a mixture of antimony sulphide and red phosphorus. Safety matches may also be ignited by drawing them quickly over a sheet of glass or linoleum.

HYDRIDES OF PHOSPHORUS

There are three hydrides of phosphorus—

Gaseous phosphoretted hydrogen or phosphine, PH_3.

Liquid phosphoreted hydrogen, P_2H_4.

Solid phosphoretted hydrogen, P_4H_2.

Phosphine, PH_3, is made by heating small pieces of yellow phosphorus with fairly strong caustic soda solution in a flask, from which the air has been completely displaced by means of coal gas. See Fig. 100.

The gas may be collected over water. The reaction which takes place may be represented by the equation—

$$3NaOH + 4P + 3H_2O = 3NaH_2PO_2 + PH_3$$

Sodium hypophosphite

At the end of the experiment the phosphine in the flask must be completely displaced by coal gas before air is admitted.

Prepared in this way the phosphine contains some liquid phosphoretted hydrogen, which makes the gas spontaneously inflammable in contact with the air. Each bubble of the gas, as it escapes from the water, burns with a bright flame and produces a vortex ring of white fumes of metaphosphoric acid. If the gas is first passed through a tube cooled in a freezing mixture, liquid phosphoretted hydrogen is condensed, and the issuing phosphine is no longer spontaneously inflammable. When the liquid phosphine is exposed to sunlight, it is converted into gaseous phosphine and a solid, which is supposed to have the composition P_4H_2.

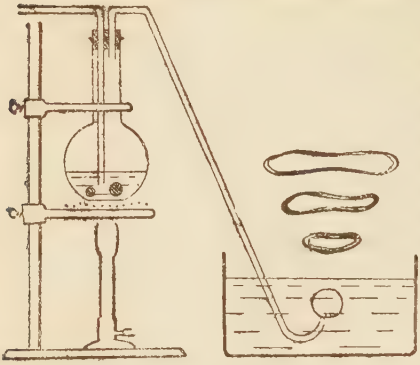


FIG. 100

The hydrides of phosphorus may also be obtained by the action of water on calcium phosphide.

$$3P_2Ca_2 + 12H_2O = 6Ca(OH)_2 + 4PH_3 + 2P$$

Phosphine can also be obtained by the action of caustic soda solution on phosphonium iodide.

$$PH_4I + NaOH = NaI + PH_3 + H_2O$$

Phosphonium iodide

Compare $NH_4Cl + NaOH = NaCl + NH_3 + H_2O$

Ammonium chloride

Properties—Gaseous phosphine is a colourless gas which has an unpleasant smell, somewhat like that of decaying fish. It is very poisonous. It is not spontaneously inflammable. Its ignition temperature is, however, only 100° C. It burns readily with a bright flame, with formation of water and metaphosphoric acid.

$$PH_3 + 2O_2 = HPO_3 + H_2O$$

It differs therefore from ammonia, which does not burn in air. It differs from ammonia also in solubility, action on litmus, and behaviour when heated. It is only slightly

soluble in water, has no action on litmus, and is readily decomposed into its elements by heat.

When collected over mercury and subjected to the electric discharge, two volumes of phosphine give solid phosphorus and three volumes of hydrogen. Therefore a molecule of phosphine contains a molecule and a half, *i.e.* three atoms, of hydrogen.

∴ The formula is PH_3, P_2H_3, or P_xH_3.

The vapour density of phosphine is 17. Therefore its molecular weight is 34.

∴ A molecule of phosphine contains 31 of phosphorus, or one atom of phosphorus.

∴ The formula is PH_3.

Phosphine will combine with acids, at low temperatures and in absence of water, to form phosphonium salts, analogous to ammonium salts.

$PH_3 + HI = PH_4I$ Phosphonium iodide

$2PH_3 + H_2SO_4 = (PH_4)_2SO_4$ Phosphonium sulphate

Phosphonium chloride and bromide can also be obtained.

These salts are only stable at low temperatures, and they are readily decomposed by water and alkalis, with evolution of phosphine.

$$PH_4Br + NaOH = PH_3 + NaBr + H_2O$$

OXIDES AND OXYACIDS OF PHOSPHORUS

OXIDES

Phosphorus suboxide, P_4O
Phosphorous oxide, P_4O_6
Phosphorus tetroxide, P_2O_4
Phosphorus pentoxide, P_4O_{10}

ACIDS

Hypophosphorous acid, $PH(OH)_2$ or H_3PO_2
Phosphorous acid, $P(OH)_3$ or H_3PO_3
Hypophosphoric acid, $P_2O_2(OH)_4$ or $H_4P_2O_6$
Orthophosphoric acid, $PO(OH)_3$ or H_3PO_4
Pyrophosphoric acid, $P_2O_3(OH)_4$ or $H_4P_2O_7$
Metaphosphoric acid, $PO_2(OH)$ or HPO_3

Of the oxides and acids mentioned above, it will only be necessary for us to deal with the more important, viz. phosphorous and phosphoric oxides and acids.

Phosphorous oxide, P_4O_6

This oxide is obtained by burning phosphorus in a limited supply of air by means of the apparatus shown in Fig 101.

Yellow phosphorus is placed in the glass tube **A**, which is

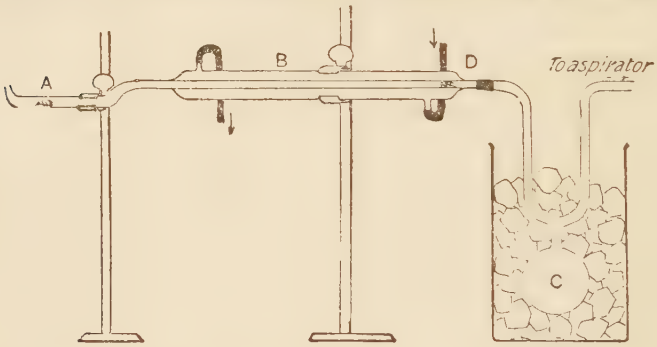


FIG. 101

connected to the Liebig condenser **B**, through which passes a stream of water at 60° C. At **D** is placed a plug of asbestos to prevent the passage of any phosphorus pentoxide which may be found. The phosphorous oxide is condensed in the bulb **C**, which is immersed in a freezing mixture. The phosphorus in **A** is lighted, and a gentle stream of air is sucked through the apparatus by means of an aspirator.

Properties—Phosphorous oxide is a snow-white crystalline solid, which melts at 22° C. to a colourless liquid boiling at 173° C. It smells like garlic. The oxide slowly dissolves in cold water, forming phosphorous acid.

$$P_4O_6 + 6H_2O = 4H_3PO_3$$

With hot water it gives spontaneously inflammable phosphoretted hydrogen, and a red solid, which is probably a mixture of red phosphorus and phosphorus suboxide.

When exposed to air, it is slowly oxidised to phosphorus pentoxide. Its vapour density is 110. Therefore its molecular weight is 220, corresponding to the formula P_4O_6.

Phosphorous acid, $P(OH)_3$ or H_3PO_3

This acid is formed when phosphorous oxide is dissolved in cold water.

It is readily prepared by adding phosphorus trichloride to excess of cold water.

$$PCl_3 + 3H_2O = P(OH)_3 + 3HCl$$

The liquid is concentrated until its temperature is 180°C., and is then allowed to cool, when it solidifies to a crystalline solid.

Properties—A white crystalline solid, which melts at 70° C. The solution will reduce silver salts to metallic silver, and mercuric chloride to mercuous chloride.

$$2HgCl_2 + H_3PO_3 + H_2O = 2HgCl + H_3PO_4 + 2HCl$$

Mercuric chloride — Mercurous chloride

When phosphorous acid is heated, it decomposes, giving phosphoretted hydrogen and phosphoric acid.

$$4H_3PO_3 = 3H_3PO_4 + PH_3$$

It is a tribasic acid, but its normal salts are not as stable as the salts in which one acid hydrogen atom is still unreplaced.

Thus, Na_3PO_3 is decomposed by water.

$$Na_3PO_3 + H_2O = Na_2HPO_3 + NaOH$$

Phosphorus pentoxide, P_4O_{10}

This oxide may be obtained by burning phosphorus in a small dish, placed on a glass plate and covered with a bell jar. Fig. 102.

Properties—It is a white, amorphous, bulky solid, without smell. As usually obtained it smells slightly of garlic, owing to the presence of some impurity of phosphorous oxide. It very readily absorbs moisture from the air or from gases, and is therefore most useful for drying gases.

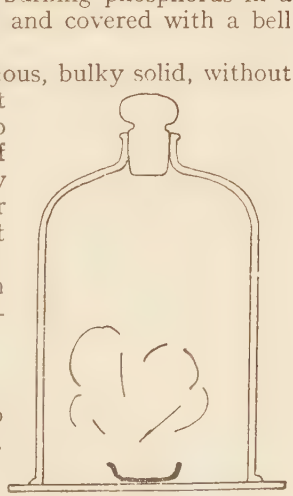


FIG. 102

It dissolves in cold water with a hissing noise, forming metaphosphoric acid.

$$P_4O_{10} + 2H_2O = 4HPO_3$$

This acid gradually changes to orthophosphoric acid on standing. Boiling makes the change rapid.

$$HPO_3 + H_2O = H_3PO_4$$

Orthophosphoric acid, $PO(OH)_3$ or H_3PO_4

Formation—

(1) A solution of this acid is obtained when phosphorus pentoxide is dissolved in boiling water.

$$P_4O_{10}+6H_2O=4H_3PO_4$$

(2) It is readily prepared by oxidation of red phosphorus with strong nitric acid.

$$4P+10HNO_3+H_2O=4H_3PO_4+5NO_2+5NO$$

(3) On the large scale phosphoric acid is obtained by treatment of bone ash with strong sulphuric acid.

$$Ca_3(PO_4)_2+3H_2SO_4=3CaSO_4+2H_3PO_4$$

The liquid is filtered from precipitated calcium sulphate, heated to a temperature of 140° C., and allowed to cool.

Properties—Phosphoric acid crystallises in six-sided rhombic prisms, which melt at 38° C. It is deliquescent.

The acid is tribasic, and therefore forms three series of salts—

Na_3PO_4	Normal sodium phosphate
Na_2HPO_4	Disodium hydrogen phosphate
NaH_2PO_4	Sodium dihydrogen phosphate

Neutralisation of phosphoric acid with alkalis gives the mono-hydrogen salts. Na_3PO_4 is alkaline to indicators. NaH_2PO_4 is acid to indicators.

An important phosphate is microcosmic salt, $HNa(NH_4)PO_4$. Part of the hydrogen of the acid has been replaced by sodium and part by ammonium.

With the exception of phosphates of the alkali metals, sodium, potassium, etc., the phosphates of the metals are insoluble in water. They are readily precipitated by addition of a soluble phosphate to a solution of a soluble salt of the metal. Where free acid is produced in the reaction, complete precipitation will only take place on neutralisation of the acid.

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3$$

Insoluble silver phosphate — Free acid

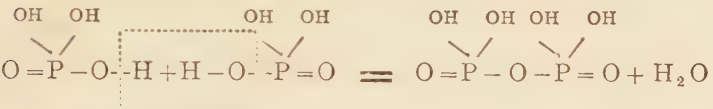
$$2Na_3PO_4+3CaCl_2=Ca_3(PO_4)_2+6NaCl$$

Pyrophosphoric acid, $H_4P_2O_7$ or $P_2O_3(OH)_4$

The acid is obtained by heating orthophosphoric acid to 214°.

$$2H_3PO_4=H_4P_2O_7+H_2O$$

The reaction may be written—



Properties—The acid is an opaque crystalline solid, which is soluble in water. When the solution is boiled, it rapidly changes to orthophosphoric acid.

$$H_4P_2O_7 + H_2O = 2H_3PO_4$$

This change also takes place slowly in the cold.

The acid is tetrabasic. It forms soluble salts with the alkali metals and insoluble salts with other metals. Pyrophosphates can be obtained by strongly heating monohydrogen phosphates, or phosphates in which one hydrogen atom has been replaced by ammonium (NH_4) and the other hydrogen atoms by metals.

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O$$
$$2MgNH_4PO_4 = Mg_2P_2O_7 + H_2O + 2NH_3$$

Magnesium ammonium phosphate — Magnesium pyrophosphate

Metaphosphoric acid, PO_2OH or HPO_3

This acid is obtained by strongly heating orthophosphoric acid or pyrophosphoric acid.

$$H_3PO_4 = HPO_3 + H_2O$$
$$H_4P_2O_7 = 2HPO_3 + H_2O$$

Properties—The acid is often called *glacial phosphoric acid.* In appearance it is very similar to ice.

It is readily soluble in water, and its solution is rapidly converted into orthophosphoric acid on boiling.

$$HPO_3 + H_2O = H_3PO_4$$

The change takes place slowly in the cold.

The acid is monobasic. Metaphosphates are obtained by strongly heating the dihydrogen phosphates.

$$NaH_2PO_4 = NaPO_3 + H_2O$$

The phosphoric acids can readily be distinguished from one another :—

Reagent	Orthophosphoric Acid	Pyrophosphoric Acid	Metaphosphoric Acid
Albumen	No change	No change	Coagulation of the albumen
Silver nitrate solution to a neutral solution of the acid	Yellow precipitate of Ag_3PO_4	White crystalline precipitate of $Ag_4P_2O_7$	White gelatinous precipitate of $AgPO_3$

Warmed with nitric acid and excess of ammonium molybdate solution, any phosphate will give a yellow precipitate of ammonium phospho-molybdate which has the approximate composition, $2(NH_4)_3PO_4.22MoO_3.12H_2O$.

PHOSPHORUS AND CHLORINE

Phosphorus trichloride, PCl_3

Preparation—Pass dry chlorine over red phosphorus, gently warmed in a retort. See Fig. 103.

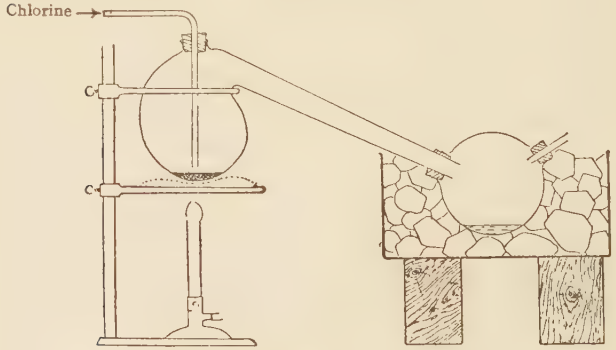


FIG. 103

The phosphorus trichloride is condensed in a well-cooled receiver, and the excess of chlorine is conducted to a draught chamber.

Properties—Phosphorus trichloride is a colourless, mobile liquid, with a pungent smell. It boils at 76° C. It fumes

strongly in moist air. It is decomposed by water, forming phosphorous acid and hydrochloric acid.

$$PCl_3 + 3H_2O = P(OH)_3 + 3HCl$$

Its vapour density is nearly 69, corresponding to the formula PCl_3.

Phosphorus pentachloride, PCl_5

Preparation—Pass excess of dry chlorine over the surface of cooled phosphorus trichloride.

$$PCl_3 + Cl_2 = PCl_5$$

Properties—It is a pale yellow, crystalline solid, which melts under pressure at 148° C. It has a pungent smell, and fumes strongly in moist air. With a small quantity of water it forms phosphorus oxychloride and hydrochloric acid.

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

With excess of water it forms a mixture of phosphoric and hydrochloric acids.

$$PCl_5 + 4H_2O = PO(OH)_3 + 5HCl$$

The density of the vapour of phosphorus pentachloride is abnormal. When vaporised it splits up into a mixture of equal volumes of phosphorus trichloride vapour and chlorine. Thus its density, when dissociation is complete at 300° C., is only half that corresponding to the formula PCl_5.

PCl_5	=	PCl_3	+	Cl_2
2 volumes		2 volumes		2 volumes

Density of $PCl_3 = \frac{31 + 106.5}{2} = 68.75$.

Density of $Cl_2 = \frac{71}{2} = 35.5$.

Mean of densities of PCl_3 and $Cl_2 = \frac{68.75 + 35.5}{2} = 52.12$.

This value, 52.12, is the density of the vapour of phosphorus pentachloride at 300° C. The vapour of phosphorus pentachloride is therefore dissociated, on heating, into equal volumes of chlorine and phosphorus trichloride vapour.

Phosphorus pentachloride is much used as a test for the presence of a hydroxyl (OH) group in the molecule of organic compounds. Thus—

$C_2H_5.OH$	+	PCL_5	=	$C_2H_5.Cl$	+	$POCl_3$	+	HCl
Alcohol				Ethyl chloride				

$CH_3.CO.OH + PCl_5 = CH_3.CO.Cl + POCl_3 + HCl$
Acetic acid — Acetyl chloride

The OH of the compound is replaced by a chlorine atom, phosphorus oxychloride is formed, and hydrochloric acid is given off.

Phosphorus forms similar compounds with the other halogens. Thus compounds of the formulæ PBr_3, PBr_5, P_2I_4, PI_3, PF_3, and PF_5 are known.

PRACTICAL EXERCISE

Find out if the salts A, B, C are orthophosphates, pyrophosphates, metaphosphates, or phosphites.

CHAPTER XXIII

CARBON AND ITS OXIDES

Exp. 149—To make various forms of carbon and investigate their properties

Directions—

(1) Make wood charcoal by heating wood in a test-tube.

(2) Make animal charcoal by heating pieces of bone in a test-tube.

(3) Make coke by heating coal in a test-tube.

(4) Make sugar charcoal from sugar in a similar way.

(5) Obtain graphite from iron filings by dissolving the filings in dilute sulphuric acid, filtering and washing the residue with water. (You will probably require, for the tests below, more graphite than you obtain in this way.)

Carry out the following tests with each of your specimens :—

(*a*) Test the hardness with your finger nail, and try if the substance will mark paper.

(*b*) Try whether the specimen will float on water. If it floats, powder a portion finely, and shake it with water in a test-tube. Explain the result.

(*c*) Heat portions of each specimen strongly in the air on platinum foil, or on iron spoons. Note the relative amount of ash obtained from each.

(*d*) Boil with dilute hydrochloric acid. Filter if necessary. Heat the residue strongly in the air, and notice the effect that the hydrochloric acid has had on the amount of ash left.

Exp. 150—To decolorise litmus solution

Directions—Boil for some minutes about 50 c.c. of weak litmus solution with a few grams of animal charcoal. Filter.

Exp. 151—To show the absorption of offensive gases by charcoal

Directions—Place a piece of meat (putrid if possible) in a gas jar and fill the jar with broken charcoal. Leave it for some days, and notice whether any offensive smell escapes from the jar.

Exp. 152—To show that carbon dioxide is produced when any of the forms of carbon is oxidised

Directions—Fit up an apparatus, such that air may be drawn or driven over strongly heated charcoal or graphite and afterwards through lime-water. Try the experiment with (*a*) charcoal, (*b*) graphite.

If no result is obtained with graphite, mix finely powdered graphite with twice its weight of potassium chlorate (to provide oxygen for the burning of the graphite), heat strongly, and pass the gases produced through lime-water.

Exp. 153—To obtain specimens of metals by reducing metallic salts with charcoal

Directions—Make a shallow hole in a block of charcoal, put into it a pinch of the finely powdered salt, and heat the salt strongly with the mouth blow-pipe. Blow through the luminous flame of the bunsen burner.

If you cannot obtain a bead of the metal, mix the salt with its own bulk of sodium carbonate and heat again. The sodium carbonate melts and brings the salt into close contact with the charcoal.

By this means you can obtain the metals copper, lead, silver, tin, bismuth, and antimony from their salts. With tin compounds a metallic bead is obtained only with difficulty unless a powerful reducing agent, such as potassium cyanide, is mixed with the salt.

Exp.154—To prepare carbon dioxide and examine its properties

Directions—Prepare carbon dioxide by treating a carbonate (marble is the best substance to use) with dilute hydrochloric acid. Collect the gas by downward displacement.

Determine the properties in the ordinary way.

In addition carry out the following experiments :—

(1) Pass the gas through about 200 c.c. of lime-water, filter, and to the solid obtained add acid. Test the gas evolved.

(2) Pass the gas through a small quantity of diluted lime-water for some time. Explain the result. Heat some of the clear liquid obtained, and test any gas evolved.

(3) Try to obtain crystals of sodium carbonate by passing the gas into caustic soda solution and evaporating the solution you obtain. Carefully think out the details of the experiment before you begin. Decide for yourself whether the solution of caustic soda is to be strong or dilute, and the way by which you will tell when enough carbon dioxide has been passed.

Exp. 155—To obtain carbon monoxide from carbon dioxide

Directions—Pass, very slowly, a current of carbon dioxide through a narrow hard glass tube packed with charcoal. Fig. 104. Heat the tube strongly. The top of the tube

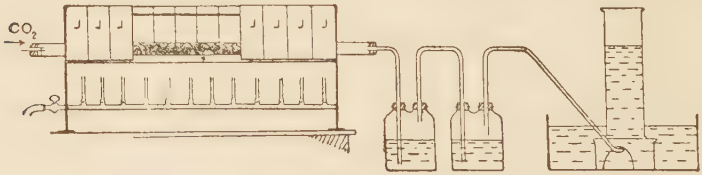


FIG. 104

should be covered with a strip of asbestos board. Wash the gas free from carbon dioxide by passing it through strong caustic soda solution. Collect the carbon monoxide over water. Test the gas with a lighted taper.

Exp. 156—To prepare carbon monoxide and examine its properties

Caution—Carbon monoxide is very poisonous. This experiment should therefore be carried out in a draught chamber.

Directions—Carefully heat in a flask about 20 grams of crystallised oxalic acid with three times its volume of strong sulphuric acid. Pass the mixture of carbon dioxide and

carbon monoxide obtained through a wash-bottle containing strong caustic soda solution. Collect over water.

Examine the gas in the usual way, but do not smell it. In addition, fill a test-tube with the gas and invert it in an evaporating basin containing cuprous chloride dissolved in ammonia solution. Allow to stand for some time. Does the gas dissolve?

Finally pass carbon monoxide over strongly heated cupric oxide. Is the oxide reduced to metal?

CARBON. Symbol, C

Carbon is found free in nature in each of its three chief forms, viz.: diamond, its crystalline form; graphite, its semi-crystalline form; and charcoal, its amorphous form.

Combined with oxygen, it occurs as carbon dioxide in the air and in many natural waters; combined with metals and oxygen, it occurs widely as carbonates, such as limestone, dolomite, magnesite. It is an essential constituent of all animal and vegetable substances, and it is present in considerable proportion in mineral oils. Coal is an impure form of carbon.

DIAMOND

This substance is found in various parts of India, Brazil, South Africa, and Australia. In India it is found mainly in river gravel and deposits on the surface of the ground. In South Africa it occurs at Kimberley in what is known as the "blue earth." Diamond may be colourless, pink, blue, green, grey, or black. Its mode of origin is unknown.

For its artificial preparation high temperature and pressure are necessary. Moissan, a French chemist, succeeded in preparing small diamonds. He packed pure charcoal into the middle of a cylinder of iron, and closed it in with a plug of the same metal. This cylinder he placed in molten iron, contained in a crucible, which was heated to about 3000° C. in the electric furnace, and afterwards suddenly cooled by being plunged into molten lead. The lead cooled the crucible more quickly than water would have done. An enormous pressure was exerted by the solid outer coating of iron on the inner portion of the iron which was still exceedingly hot. Thus the charcoal was subjected at the same time to great pressure and high temperature. When the mass of iron was dissolved away by acids, small crystalline fragments of diamond were found.

Properties—Diamond, when pure, is a colourless crystalline substance. It crystallises in the cubic system, the crystals being usually of an octahedral type. See Fig. 105.

Its specific gravity is about 3.5.

It is the hardest substance known, and is therefore very useful for cutting glass, and for boring, grinding, and polishing hard substances. For these purposes the dark impure forms, carbonado, bort, etc., are used. The best specimens of diamond are used as gems. The beauty of the gem is due to its high refractive index, which is higher than that of any other substance.

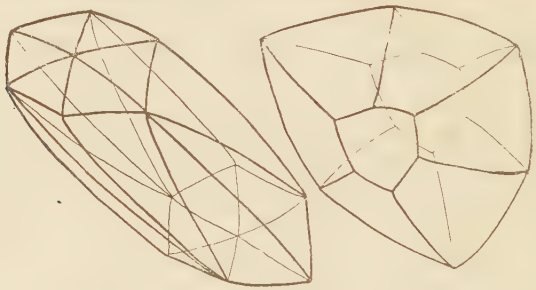


FIG. 105

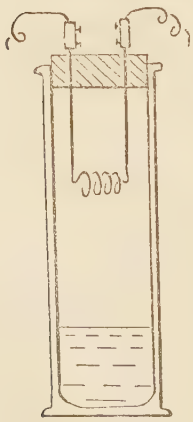


FIG. 106

Diamond is very brittle. It is infusible. It will burn when strongly heated in air or ogygen, giving carbon dioxide, and leaving a very small quantity of ash. The burning of diamond may be carried out in the apparatus shown in Fig. 106. The cylinder contains oxygen and a few c.c. of clear lime-water at the bottom. Through the india-rubber cork pass two thick copper wires, the lower ends of which are connected together by a spiral of thin platinum wire. In the spiral is placed a fragment of diamond. The platinum wire is then made white hot by the passage of an electric current. When the diamond begins to burn, the current is shut off, and the diamond continues to burn brilliantly with formation of carbon dioxide.

GRAPHITE (*Black-lead, plumbago*)

This form of carbon is much more plentiful than diamond. It occurs in large quantities in Ceylon, Siberia, India, and California.

It is manufactured at Niagara by *Acheson's Process.* A powerful electric current is passed between carbon rods through a mixture of powdered coke, a little pitch and a little sand, contained in a brick furnace, the bottom of which is protected by sand. After about thirty hours the coke is converted to a soft, pure graphite.

Properties—Graphite is a soft, greyish-black substance, which has a metallic lustre, and is soapy to the touch. It is believed to crystallise in the rhombohedral system. Its specific gravity is about 2.5. It is a good conductor of heat and electricity.

When heated strongly in oxygen, graphite burns, giving carbon dioxide and a small quantity of ash. The easiest way to burn it is to heat finely powdered graphite with twice its weight of potassium chlorate. The graphite combines with the oxygen of the potassium chlorate with incandescence.

The name *graphite* is derived from the Greek γράφω = *I write.* The names *black-lead* and *plumbago* owe their origin to the old and erroneous supposition that graphite contained lead.

Graphite is prepared for use in black-lead pencils by grinding the natural substance to powder and washing the powder free from gritty matter. It is then mixed with fine washed clay, and forced through perforated plates.

Graphite is used for making plumbago crucibles, for polishing gunpowder, as a coating for iron to prevent rusting, and as a lubricant for machinery in which oil cannot be used.

Graphite may be distinguished, chemically, from diamond and amorphous carbon by repeated treatment with a mixture of fuming nitric acid and potassium chlorate. Under such treatment it forms a solid compound containing hydrogen and oxygen and known as graphitic acid, whereas under similar treatment diamond is unchanged, and amorphous carbon is completely oxidised away.

AMORPHOUS CARBON

This allotropic modification of carbon is familiar to us in several forms. Sugar charcoal, lampblack or soot, charcoal,

gas carbon, coke, animal charcoal, and coal, are all more or less impure forms of amorphous carbon.

Sugar charcoal is the purest form of amorphous carbon.

It is best obtained by heating pure white sugar in a covered crucible, and afterwards in a stream of pure chlorine. Its specific gravity is 1.57. It is black, infusible, and insoluble. It is tasteless, and has no smell. When burnt, it leaves a very small quantity of ash.

Charcoal or wood charcoal is prepared on the large scale by the destructive distillation of wood from large ovens. The volatile products, consisting of water, pyroligneous acid, wood spirit, acetone, and tar, are condensed, separated, and made use of.

The old process of charcoal-burning is still used in countries where wood is plentiful. The wood is built up into large conical heaps and covered over with turf, openings being left at the bottom for the inlet of air, and a space up the middle for the escape of the gases. The heap is then lighted, and the air admitted is carefully regulated in order to carbonise the wood as slowly as possible. The valuable volatile products are completely lost in this process.

Properties—Good charcoal is pure black in colour, and has a bright fracture. It burns in air without flame or smoke, leaving a small quantity of ash. It is very porous. When its pores are filled with air its specific gravity varies from .1 to .2, according to the wood used for its preparation. If a piece of charcoal is floated on water and the air in the vessel is pumped out, the charcoal sinks as soon as the air has been drawn out from its pores. Finely powdered charcoal sinks in water, owing to lack of enclosed air. The true specific gravity of charcoal is about 1.5.

Charcoal is a bad conductor of heat and electricity. It has a remarkable power of absorption of gases, which are easily liquefied. Thus, if a piece of freshly made cocoa-nut-shell charcoal is introduced into a tube of ammonia standing in a trough of mercury, the ammonia is rapidly absorbed. Hunter has found that cocoa-nut-shell charcoal will absorb about 170 times its volume of ammonia. Hydrochloric acid gas, sulphur dioxide, carbon dioxide, and even oxygen are also absorbed, but in smaller quantities than ammonia.

Offensive gases are absorbed by charcoal, and in the pores

of the charcoal these gases are oxidised by the oxygen of the air, which is also absorbed. Consequently, sewer ventilators are sometimes packed with charcoal to prevent the escape of bad-smelling gases.

Animal charcoal (*Bone black*)

This form of carbon is made by destructive distillation of bones. It contains only about 10 per cent of carbon, the remainder consisting mainly of calcium phosphate. It absorbs colouring matters from solution. Thus, if red wine, litmus solution, indigo solution, or brown sugar solution be warmed with animal charcoal and filtered, the filtrate is quite colourless. Animal charcoal is therefore used for the refining of brown sugar.

Lampblack is made by burning substances rich in carbon, *e.g.* turpentine, paraffin, etc., in a limited supply of air. The lampblack or soot is collected in chambers in which are hung coarse blankets. Lampblack always contains hydrogen. The hydrogen can, however, be removed by heating the soot in a current of chlorine. A very pure form of carbon is left.

Lampblack is used for making black paint and printer's ink.

Coke is the hard substance left behind when coal is distilled. It contains about 90 per cent. of carbon (the remainder consisting of what would be the ash if the coal were completely burnt), together with small quantities of hydrogen, oxygen, and nitrogen.

Coke is generally hard and lustrous. As a fuel it gives no smoke, and it produces a higher temperature than common coal.

Gas carbon is the hard deposit which collects on the top and sides of the retorts used in coal gas manufacture. It is very hard, fairly pure, and a good conductor of electricity. It is used largely for making carbon rods for the electric arc light.

Coal

When vegetable matter decays in absence of air, either under water or under deposits of sand and mud, the impure form of carbon known as coal is formed. During this process of decay, some of the carbon, hydrogen, and oxygen present in the vegetable tissue escape as marsh gas and carbon dioxide.

This is evident from the presence of these two gases, often highly compressed, in the coal measures.

The great seams of coal were mainly formed during the geological period known as the Carboniferous period. Many seams were produced by the burying of the luxuriant vegetation, consisting largely of tree ferns, which flourished on the flat, low-lying, marshy tracts bordering the coasts. Very slow sinking of the land caused these tracts to be covered with masses of sand and mud from the waste of the land by river and sea. When subsidence stopped, land was gradually formed once more by the silting up of the shallow sea, and vegetation sprang up. When the sinking began again the new mass of vegetation was buried under sediment, and a second coal seam was in course of time produced. In this way coal seam above coal seam might be formed.

Other seams were probably formed by the covering up of driftwood by the sediment of the sea.

Peat and lignite or brown coal may be regarded as stages in the production of coal.

Soft or bituminous coals are used for the manufacture of coal gas and for domestic purposes. They burn with a very smoky flame, and give off large quantities of inflammable gases.

Hard coal or anthracite is much harder, is more difficult to light, gives great heat when burned, and produces very little flame and smoke. It is used largely as a naval coal.

The following table shows the composition of several classes of coal :—

	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur	Ash	Water
Bituminous coal (Northumberland)	78.69	6.00	10.07	2.37	1.51	1.36	—
Bituminous coal (S. Wales)	83.44	5.71	5.93	1.66	0.81	2.45	—
Anthracite coal (S. Wales)	92.56	3.33	2.53	—	—	1.58	—
Anthracite coal (Pennsylvania)	92.59	2.63	1.61	0.92	—	2.25	—

Peat contains, when dried, about 15 to 20 per cent. of

water. It is constantly being formed by the decomposition of marsh plants.

Lignite or brown coal is brown in colour, and often shows a woody structure. It is composed of the remains of trees and shrubs, ash, poplar, etc., and is therefore of much more recent origin than common coal.

Some general properties of carbon—Atomic weight = 12. Molecular weight unknown. Vapour density unknown.

Carbon in any of its forms can be made to combine with oxygen; in the amorphous state it combines at a comparatively low temperature, but in the form of graphite and diamond, strong heating is necessary before it combines with oxygen.

Whatever form of carbon is used, it gives, if pure, the same weight of carbon dioxide and no other product.

It would be a good exercise for the student to devise, draw, and, if possible, use apparatus suitable for burning charcoal, graphite, and diamond in oxygen, and proving that equal weights of carbon give equal weights of carbon dioxide.

One of the most useful properties of carbon is its power of reduction. Many metallic oxides, when heated strongly with charcoal, are reduced to metal. This property is made use of in the laboratory in blow-pipe analysis. Salts of lead, silver, copper, bismuth, antimony, and tin, when mixed with sodium carbonate as a flux, and heated on charcoal with the mouth blow-pipe, give metallic beads. Magnetic metallic powders of iron, cobalt, and nickel can, in a similar way, be obtained from salts of these metals. The salt in each case is converted by the action of the sodium carbonate and heat into the oxide, which is reduced to metal by means of the hot charcoal and the reducing gases of the flame.

$$PbO + C = Pb + CO$$
$$CuO + C = Cu + CO$$

The reducing action of carbon is made use of in the extraction of many of the metals, *e.g.* iron and zinc.

$$Fe_2O_3 + 3C = 2Fe + 3CO$$
$$ZnO + C = Zn + CO$$

Red-hot charcoal combines directly with sulphur vapour, forming carbon bisulphide (*q.v.*), $C + S_2 = CS_2$.

It will not combine directly with the halogens or with

nitrogen. It can be made to combine directly with hydrogen, by passing a stream of hydrogen through a globe in which an electric arc is formed between two carbon rods. In this way very small quantities of acetylene (C_2H_2) are formed.

$$2C + H_2 = C_2H_2$$

CARBON DIOXIDE, CO_2

History—Van Helmont, in the seventeenth century, showed that carbon dioxide was formed during fermentation and combustion. He called it *gas sylvestre*. Black, in the eighteenth century, showed that it was a constituent of the alkaline carbonates (mild alkalis), and so gave it the name *fixed air*. Lavoisier proved it to be an oxide of carbon.

Occurrence—Carbon dioxide is present in air to the extent of 3 volumes in 10,000 volumes of air. It occurs dissolved in all natural waters, and it occurs in considerable quantity in the natural effervescing waters. Processes of decay, fermentation and combustion send into the air enormous quantities of the gas, and still larger quantities of it issue from cracks and fissures in volcanic regions. The Grotto del Cane, near Naples, owes its name to the fact that a dog, on entering the cave, is suffocated by the layer of carbon dioxide on the floor of the cave, whereas a man, whose head is above the gas, can enter the cave with impunity.

Formation—(1) Carbon dioxide can be made from its elements by burning carbon in a free supply of air or oxygen.

$$C + O_2 = CO_2$$

(2) The gas can also be obtained by strongly heating potassium and sodium bicarbonates, limestone, or chalk, or other carbonates.

$$2KHCO_3 = K_2CO_3 + CO_2 + H_2O$$
$$CaCO_3 = CaO + CO_2$$
$$MgCO_3 = MgO + CO_2$$

Lime is made on a large scale by heating limestone or chalk very strongly in kilns. If the carbon dioxide is not removed as it is formed, only a portion of the calcium carbonate is decomposed, and, on cooling, even this portion is re-formed from the lime and carbon dioxide. We have here

therefore, another example of *dissociation*. The change may be expressed—

$$CaCO_3 \rightleftarrows CaO + CO_2$$

(3) Carbon dioxide is prepared in the laboratory by the action of dilute cold hydrochloric or nitric acid on marble. Sulphuric acid cannot be used, owing to the formation of a coating of insoluble calcium sulphate on the marble. This coating quickly stops the action. But this difficulty can be avoided by the use of finely powdered chalk instead of marble. The gas is collected by downward displacement of air.

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

(4) Enormous quantities of carbon dioxide are evolved in brewing beer. These were formerly wasted. They are now washed, purified, and compressed into strong steel cylinders. In these cylinders, carbon dioxide comes into market in the liquid state.

Properties—Molecular weight = 44. Density = 22. Boiling-point = −78° C. Liquefied at 15° C. by 52 atmospheres pressure. 1.8 c.c. of the gas dissolve in 1 c.c. of water at 0° C.

Carbon dioxide is a colourless gas with a faint, sharp smell. It is about 1½ times as heavy as air. It may therefore be collected by downward displacement. A soap bubble filled with air floats on carbon dioxide contained in a large vessel. See Fig. 107.

At ordinary temperatures water dissolves about its own volume of the gas.

Carbon dioxide is liquefied by a pressure of 36 atmospheres at 0° C. to a colourless, mobile liquid, which will float on water without mixing. When warmed, the liquid expands more than a gas.

Thus, 100 volumes of the liquid at 0° C. becomes 114 volumes at 20° C., whereas 100

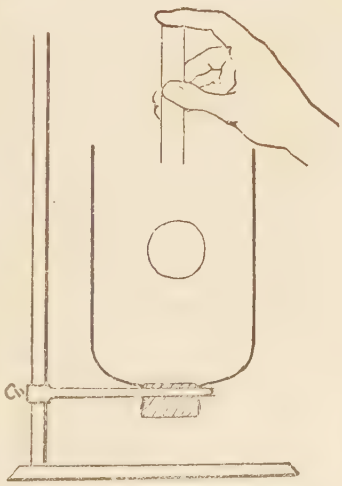


FIG. 107

volumes of air at 0° C. become only 107.3 volumes at 20° C. When liquid carbon dioxide is allowed to issue into the air from a fine jet, the heat absorbed in the evaporation causes a portion of the liquid to solidify as a snow-like solid. The solid volatilises, but not as quickly as the liquid evaporates. When a solution of solid carbon dioxide in ether is made to evaporate quickly, a temperature of −110° C. is obtained. Such a solution is useful, therefore, for the production of low temperatures.

Carbon dioxide will not burn, and will not support the combustion of a taper or the respiration of animals. When it is inhaled for some time, death is caused, mainly from absence of oxygen, but partly from the slightly poisonous nature of the gas. A candle will not burn in air containing 4 per cent. of carbon dioxide, and a man cannot live in such air. Even a smaller percentage of carbon dioxide is injurious.

A few metals, such as magnesium and potassium, burn brightly in the gas. Fragments of carbon and the oxide or carbonate of the metal are produced.

$$2Mg + CO_2 = 2MgO + C$$
$$4K + 3CO_2 = 2K_2CO_3 + C$$

Carbon dioxide is acid to litmus, turning it to a port wine red, and it acts towards bases like an acid oxide. For instance, when it is passed into caustic soda solution, sodium carbonate is produced, and, if the passage of the gas is continued, sodium bicarbonate is produced.

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$
$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$$

Passed into lime-water, carbon dioxide produces a milky precipitate of calcium carbonate.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

If still more gas is passed, the precipitate of chalk is redissolved as calcium bicarbonate.

$$CaCO_3 + CO_2 + H_2O = CaH_2(CO_3)_2$$

When the solution of the bicarbonate is boiled, carbon dioxide is given off and calcium carbonate is once more precipitated.

$$CaH_2(CO_3)_2 = CaCO_3 + H_2O + CO_2$$

A solution of carbon dioxide in water, therefore, acts as if it were carbonic acid, H_2CO_3. This acid has never been isolated, but many of its salts, the carbonates, are well known.

Carbon dioxide does seem to form an unstable compound with water when it has been dissolved for some time. Freshly made samples of aerated waters give off their carbon dioxide rapidly, but samples which have been kept a long time lose their gas much more slowly. Similarly the natural aerated waters, Apollinaris, Perrier, Seltzer, etc., hardly effervesce at all when opened, although they contain a considerable quantity of dissolved carbon dioxide.

Composition of carbon dioxide

(1) *Volumetric*—The volumetric composition of carbon dioxide is readily determined by means of the same apparatus as that used for the composition of sulphur dioxide. See Fig. 82. A splinter of carbon replaces the sulphur. The carbon burns in the oxygen, and, when the apparatus is once more cold, the volume of gas is found to be unchanged.

∴ Carbon dioxide contains its own volume of oxygen.

∴ A molecule of carbon dioxide contains a molecule of oxygen

" " " 2 atoms "

∴ The formula of carbon dioxide is CO_2, C_2O_2, or C_xO_2.

But the density of the gas is 22.

∴ The molecular weight is 44. The 2 oxygen atoms weigh 32.

∴ A molecule of carbon dioxide contains 12 parts of carbon or 1 atom of carbon.

∴ The formula is CO_2.

(2) *Gravimetric*—Excess of carefully purified dry oxygen is passed over strongly heated carbon, and the carbon dioxide is collected in strong caustic potash solution and weighed. A simple form of apparatus is shown in Fig. 108.

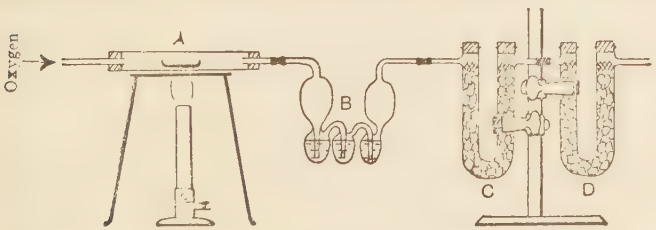


FIG. 108

A is a boat containing pure sugar charcoal.

B is a set of potash bulbs containing strong caustic potash solution to absorb the carbon dioxide produced.

C is a calcium chloride tube to absorb water vapour carried away from **B**. It is weighed with **B**.

D is a guard tube to prevent water from the air from reaching **C**.

A is weighed before and after the experiment. The weight of carbon burnt is thus found. **B** and **C** are weighed together, before and after the experiment. These weighings give the weight of carbon dioxide formed. The weight of the carbon dioxide minus the weight of the carbon burnt is the weight of the oxygen which combines with the carbon. From these weights the percentage composition of carbon dioxide can easily be calculated.

Carbonates—There are two series of carbonates, viz. the normal carbonates, obtained by the replacement of two hydrogen atoms in carbonic acid, H_2CO_3, and the acid carbonates or bicarbonates, obtained by the replacement of one hydrogen atom in the acid.

The normal carbonates are much more stable towards heat than the acid carbonates. Thus magnesium carbonate, calcium carbonate, etc., are split up only on strong heating. The bicarbonates, however, readily give up their extra carbon dioxide on gentle heating of the solids themselves or of their solutions. Normal carbonates are thus produced.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

The bicarbonates of calcium, barium, etc., are only known in solution. Those of sodium and potassium can be obtained in the solid state.

The normal carbonates of the common metals, with the exception of those of sodium, potassium, and ammonium, are all insoluble in water. Carbonates of sodium, potassium, and ammonium are alkaline to litmus.

All carbonates effervesce with acids, forming the salt of the acid, carbon dioxide, and water.

$$MgCO_3 + 2HCl = MgCl_2 + H_2O + CO_2$$
$$BaCO_3 + 2HNO_3 = Ba(NO_3)_2 + H_2O + CO_2$$

CARBON MONOXIDE, CO

History—Carbon monoxide was first obtained by Lassone in 1776 by heating zinc oxide with charcoal. For a long time

the gas was mistaken for hydrogen, and it was not until 1800 that Cruikshank showed that, when it was burned, it gave no water, and could not therefore contain hydrogen. He showed that it was an oxide of carbon.

Formation—(1) Carbon monoxide is formed when a slow stream of oxygen or carbon dioxide is passed over excess of charcoal heated to redness.

$$2C + O_2 = 2CO$$
$$CO_2 + C = 2CO$$

(2) It can be prepared by heating formic acid or a formate with strong sulphuric acid. Water is withdrawn by the sulphuric acid. $CH_2O_2 = CO + H_2O$

Formic acid

(3) It is often prepared by heating oxalic acid with excess of sulphuric acid. A mixture of equal volumes of carbon

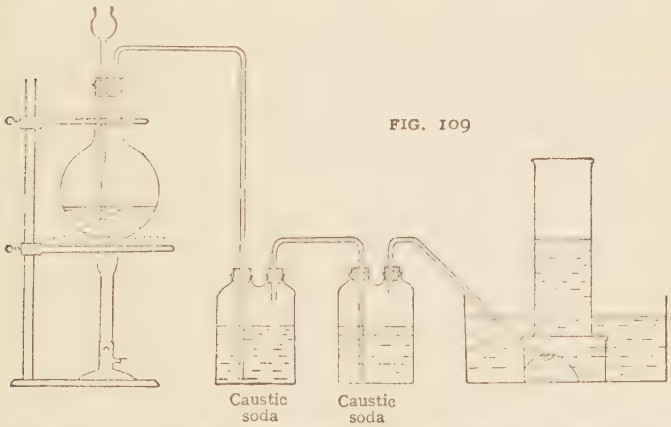


FIG. 109

dioxide and carbon monoxide is obtained. The carbon dioxide is absorbed by means of strong caustic soda solution. See Fig. 109. $C_2H_2O_4 = CO_2 + CO + H_2O$

(4) Pure carbon monoxide is prepared by heating a mixture of potassium ferrocyanide (1 part) with strong sulphuric acid (10 parts) in a large flask.

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

The water required for the reaction is obtained partly from

the commercial sulphuric acid used, and partly from the three molecules of water of crystallisation of the ferrocyanide.

Properties—Molecular weight = 28. Density = 14. Boiling-point = −190° C. 100 volumes of water at 0° C. dissolve about 3 volumes of the gas.

Carbon monoxide is a colourless, tasteless gas with a very faint smell. It is practically insoluble in water, but it is soluble in an ammoniacal solution of cuprous chloride, Cu_2Cl_2, with which it forms the compound, $Cu_2Cl_2.CO$.

It is a highly poisonous gas. Very small quantities produce headache and giddiness. Larger quantities produce insensibility and death. Its poisonous nature is due to the formation of a compound with the blood, carboxyhæmoglobin, which prevents the blood from carrying on its work of absorbing oxygen in the lungs and of distributing it through the body.

Many deaths have occurred owing to the escape of this gas from charcoal stoves and gas stoves not provided with an efficient draught. Deaths from sleeping on lime and brick kilns are probably due to carbon monoxide.

The gas burns with a bright blue flame, forming carbon dioxide. $CO + O = CO_2$

The blue flame which is often seen on a glowing coal fire is that of carbon monoxide. The carbon dioxide produced by the burning of a portion of the carbon of the coal comes into contact with more red-hot carbon, and is converted into carbon monoxide. $CO_2 + C = 2CO$

Carbon monoxide combines with chlorine in direct sunlight, forming phosgene gas or carbonyl chloride, $COCl_2$.

$$CO + Cl_2 = COCl_2$$

At high temperatures it is an excellent reducing agent. If it is passed over heated iron oxide, metallic iron is produced.

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$

Carbon monoxide is used as a fuel in the mixtures of gases known by the names *producer gas*, *water gas* and *semi-water gas*.

Producer gas contains about 30 per cent. of carbon monoxide and about 60 per cent. of nitrogen. It is prepared by driving air through white-hot coke.

Water gas contains about 40 per cent. of carbon monoxide, about 50 per cent. of hydrogen and about 5 per cent. of carbon dioxide. It is prepared by driving steam through white-hot coke.

Semi-water gas contains about 26 per cent. carbon monoxide, 50 per cent. nitrogen and 18 per cent. hydrogen. It is prepared by driving a mixture of air and steam through white-hot coke.

Composition of carbon monoxide

When 2 volumes of carbon monoxide are mixed with 1 volume of oxygen, and the mixture is exploded in a eudiometer by means of an electric spark, 2 volumes of carbon dioxide are produced.

But 2 volumes of carbon dioxide contain 2 volumes of oxygen.

Therefore, since 1 volume of free oxygen was used, the 2 volumes of carbon monoxide must have contained 1 volume of oxygen.

∴ 2 molecules of carbon monoxide contain 1 molecule or 2 atoms of oxygen.

∴ 1 molecule of carbon monoxide contains 1 atom of oxygen.

∴ The formula of carbon monoxide must be CO, C_2O, or C_xO.

The density of the gas is 14. ∴ The molecular weight is 28.

∴ In a molecule of carbon monoxide there is $28-16=12$ of carbon, *i.e.* one atom of carbon.

∴ The formula of carbon monoxide is CO.

PRACTICAL EXERCISES

(1) Find the percentage of carbon in the given specimen of animal charcoal.

(2) Determine the volume of carbon dioxide that can be obtained from one gram of the given carbonate.

(3) Determine the percentage loss of weight which occurs when sodium bicarbonate is heated.

CHAPTER XXIV

SOME SIMPLE HYDROCARBONS—COAL GAS

Exp. 157—To prepare marsh gas and investigate its properties

Directions—Mix intimately about 30 grams of sodium acetate, from which the water has been expelled by gentle heating, with about 100 grams of soda-lime (caustic soda mixed with lime). Strongly heat the mixture in a hard glass bulb or flask. Collect the gas over water and test it in the usual way.

Exp. 158—To prepare ethylene and investigate its properties

Directions—Mix about 50 c.c. of alcohol with about 200 c.c. of strong sulphuric acid, and heat the mixture in a large flask fitted with a dropping funnel and a delivery tube. Sand or broken glass should also be put into the flask to prevent frothing. The gas evolved must be washed free from carbon dioxide and sulphur dioxide by means of strong caustic soda solution, contained in one or more wash-bottles. Collect over water. Fig. 110 shows the apparatus used.

If much ethylene is wanted, a mixture of equal volumes of

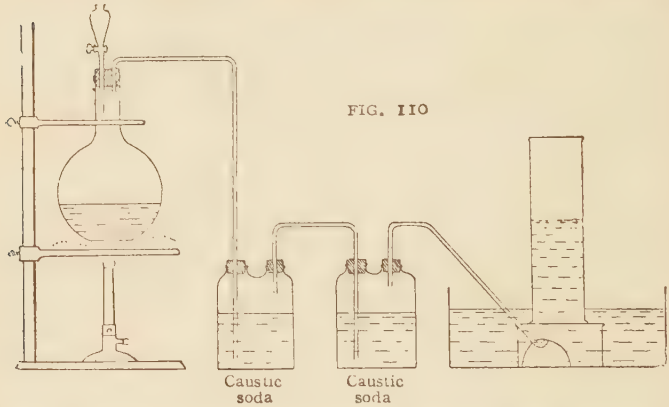


FIG. 110

strong sulphuric acid and alcohol can be run in from the dropping funnel as the evolution of gas slackens.

A better method, if phosphoric acid is available, is to heat phosphoric acid to 200° C. in a flask, and add alcohol drop by drop from a tap funnel. There is little charring or frothing, and no evolution of sulphur dioxide.

Examine the gas in the usual way.

Also pass ethylene and chlorine into a large flask and note the formation of oily drops of pleasant-smelling ethylene dichloride.

Exp. 159—To prepare acetylene and investigate its properties

Directions—Put a few pieces of calcium carbide into a small flask fitted with a dropping funnel and a delivery tube.

Run in cold water drop by drop from the funnel, and collect the acetylene over water.

Determine the properties of the gas, and carry out the following experiment :—

Pass the gas for some time into an ammoniacal solution of cuprous chloride. Filter off the reddish-brown precipitate of copper acetylide, which must not be allowed to dry. Treat the precipitate with strong hydrochloric acid and note the evolution of acetylene.

MARSH GAS (*Methane*), CH_4

Occurrence—Methane is one of the products of the decay of vegetable matter in presence of moisture. The bubbles which rise from the mud at the bottom of stagnant ponds and ditches contain much of this gas. Its occurrence in marshy districts has given the gas its name, *marsh gas*.

It is sometimes found in great quantities in coal mines. It has been produced by the slow decay of the vegetable matter, which has given rise to the coal. By miners it is called *fire-damp*.

Formation—(1) Methane is prepared by strongly heating a mixture of fused sodium acetate and soda-lime in a copper retort or a hard glass bulb. It is collected over water.

$$CH_3.COONa + NaOH = Na_2CO_3 + CH_4$$

The gas obtained by this method always contains hydrogen.

(2) A purer gas is prepared by dropping a mixture of

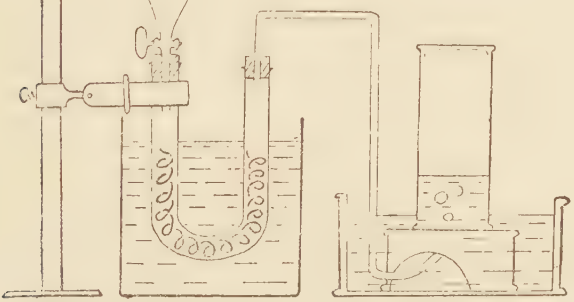


FIG. 111

equal volumes of methyl iodide (CH_3I) and methyl alcohol ($CH_3.OH$) on a zinc-copper couple. (See page 381.)

The U tube containing the zinc-copper couple is kept cool by water. See Fig. 111.

The reaction which occurs may be represented by the equation—

$$CH_3I + Zn + CH_3OH = Zn\begin{matrix}/I\\ \backslash OCH_3\end{matrix} + CH_4$$

Zinc methoxyiodide

Properties—Molecular weight = 16. Density = 8. Boiling-point = −164° C. Solubility is very slight.

Marsh gas is a colourless, odourless gas. It is insoluble in water. It is about half as heavy as air. It is very difficult to liquefy. It burns with a feebly luminous flame, and, when mixed with air or oxygen, it is explosive.

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

When one volume of marsh gas is mixed with two volumes of chlorine and the mixture is exposed to direct sunlight, after a time explosion takes place. $CH_4 + 2Cl_2 = C + 4HCl$.

When it is mixed with chlorine and exposed to the action of diffused daylight, it forms a series of compounds in which hydrogen atoms are replaced by chlorine atoms. Thus—

$CH_4 + Cl_2 = HCl + CH_3Cl$	Methyl chloride
$CH_3Cl + Cl_2 = HCl + CH_2Cl_2$	Methylene dichloride
$CH_2Cl_2 + Cl_2 = HCl + CHCl_3$	Chloroform
$CHCl_3 + Cl_2 = HCl + CCl_4$	Tetra-chlor-methane

Composition of methane—The composition of this gas is determined by exploding in a eudiometer a known volume with excess of oxygen. Carbon dioxide and water are produced. The carbon dioxide is absorbed by the introduction of strong caustic soda solution into the eudiometer. In this way the volume of the carbon dioxide and the volume of the unused oxygen are determined.

It is found that 2 volumes of methane require, for complete combustion, 4 volumes of oxygen. Two volumes of carbon dioxide are produced. The carbon dioxide contains 2 volumes of oxygen. Therefore the other 2 volumes of oxygen have gone to form water. But 2 volumes of water vapour contain 1 volume of oxygen. Therefore, if the water were in the form of steam, it would occupy 4 volumes.

Now, 2 volumes or 1 molecule of carbon dioxide contain 12 parts by weight of carbon, and 4 volumes or 2 molecules of steam contain 4 parts by weight of hydrogen.

Therefore marsh gas must contain 12 parts of carbon, *i.e.* 1 atom of carbon, combined with 4 parts of hydrogen, *i.e.* 4 atoms of hydrogen. Therefore the formula of marsh gas is CH_4.

Exercise—40 c.c of methane were exploded with 100 c.c. of oxygen. The residual gas occupied 60 c.c. When shaken with strong caustic soda solution, 40 c.c, of the residual gas were dissolved. From these data calculate the percentage composition of methane.

ETHYLENE (*Olefiant gas*), C_2H_4

Formation—Ethylene is readily prepared by heating alcohol with excess of strong sulphuric acid. Carbon dioxide and sulphur dioxide are also produced. They are separated from the gas by washing it with strong caustic soda solution. The apparatus used is shown in Fig. 110.

The following equations represent the changes which take place :—

$$C_2H_5OH + H_2SO_4 = C_2H_5.HSO_4 + H_2O$$

Alcohol — Ethyl sulphuric acid

$$C_2H_5.HSO_4 = C_2H_4 + H_2SO_4$$

Theoretically, a small quantity of sulphuric acid should convert an unlimited quantity of alcohol into ethylene. Actually, the sulphuric acid is partly diluted by the water formed in the reaction, and partly reduced to sulphur dioxide by reaction with the carbon set free.

Properties—Molecular weight = 28. Density = 14. Boiling-point = −103° C. Solubility very slight.

Ethylene is a colourless gas with a pleasant smell and sweet taste. It is almost insoluble in water. It is condensed to a liquid by a pressure of 41 atmospheres at 0° C.

It burns with a smoky, luminous flame, and, when mixed with air or oxygen in the proper proportions, it is explosive.

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$$

It combines directly with chlorine or bromine, forming the pleasant-smelling oils, ethylene dichloride and ethylene dibromide respectively.

$$C_2H_4 + Cl_2 = C_2H_4Cl_2 \qquad C_2H_4 + Br_2 = C_2H_4Br_2$$

The name *olefiant gas* (oil-making gas) is derived from this property. Ethylene is one of the chief illuminating constituents of coal gas, in which it is present in proportion varying from 4 to 10 per cent.

Composition—2 volumes of ethylene, exploded in a eudiometer with excess of oxygen, produce 4 volumes of carbon dioxide. 6 volumes of oxygen are used up. The formula of ethylene can be deduced from these facts by reasoning similar to that used for marsh gas.

ACETYLENE, C_2H_2

Formation—

(1) Acetylene is usually prepared by dropping water on calcium carbide and collecting the evolved gas over water.

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

Calcium carbide

(2) Acetylene is formed in small quantities when coal gas, marsh gas, or other hydrocarbons are burnt in a supply of air insufficient for complete combustion. These conditions are present when a bunsen burner "strikes back," *i.e.* becomes lighted at the jet near the air holes. If the gas from a burner lighted in this way is drawn through ammoniacal cuprous chloride solution, some copper acetylide is obtained. See Fig. 112.

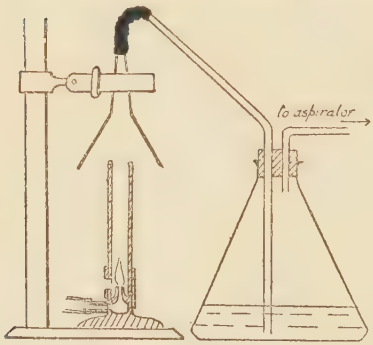


FIG. 112

Properties—Molecular weight = 26. Density = 13. One c.c. of water at ordinary temperatures dissolves about 1 c.c. of the gas. Condensed to liquid by a pressure of 50 atmospheres at 0° C.

Acetylene is a colourless gas with a disagreeable smell. It is poisonous. It is slightly lighter than air. It is fairly easily condensed to a colourless liquid.

Acetylene burns with a very bright, smoky flame, and when mixed with air or oxygen in the proper proportions (2 of

acetylene to 5 volumes of oxygen), it forms a violently explosive mixture.

$$2C_2H_2+5O_2=4CO_2+2H_2O$$

When passed into ammoniacal cuprous chloride solution, acetylene forms a brownish-red solid, called copper acetylide.

$$Cu_2Cl_2.2NH_3+H_2O+C_2H_2=2NH_4Cl+C_2H_2.Cu_2O$$

Ammoniacal cuprous chlorine — Copper acetylide

This compound, on treatment with strong hydrochloric acid, gives acetylene in a very pure state.

$$C_2H_2.Cu_2O+2HCl=C_2H_2+Cu_2Cl_2+H_2O$$

Copper acetylide, when dry, is explosive.

Acetylene combines directly with chlorine or bromine.

$C_2H_2+2Br_2=C_2H_2Br_4$ Acetylene tetrabromide

Composition—Two volumes of acetylene, exploded in a eudiometer with excess of oxygen, give four volumes of carbon dioxide. Five volumes of oxygen are used up. From these facts the formula of acetylene may be deduced by reasoning similar to that used in the case of marsh gas.

COAL GAS

Coal gas is obtained by the destructive distillation of coal. A diagram of the apparatus used is shown in Fig. 113.

Bituminous coal is heated in the ⌂ shaped retorts **A**. Coke is left behind, and the evolved gas is passed through the pipes **BB** to the hydraulic main **C**, where most of the tar collects under the water into which the pipe **B** dips. The gas is then passed by a pipe, not shown in the diagram, to the air coolers **D**, which it is made to traverse completely by means of partitions in the vessel underneath. Here most of the residual tar is deposited. The pump **E** draws the gas from the retorts and forces it through the rest of the apparatus.

The gas comes next to the tower **F**, which is filled with perforated plates, by means of which the last traces of tar are extracted. Next, it passes to the washer and scrubber **G**. In this it is exposed to a large wet surface obtained by means of wooden grids fastened to a revolving shaft. The grids are constantly wetted in the water at the bottom of the

compartments of the scrubber by the revolution of the shaft. The gas is washed from ammonia very effectually.

From the scrubber the coal gas passes through the purifiers,

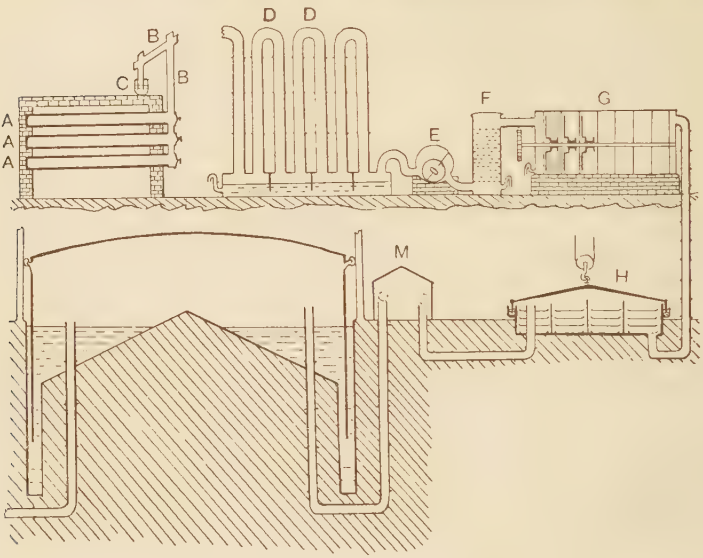


FIG. 113

of which **H** represents one. These are shallow iron boxes containing slaked lime or hydrated ferric oxide. Lime removes carbon dioxide, sulphuretted hydrogen, and carbon bisulphide vapour. Ferric hydroxide removes only sulphuretted hydrogen from the gas. Lime, although more efficient as a purifier, is expensive, and difficult to dispose of when used. The iron hydroxide can be made fresh again, *i.e. revivified*, by exposing it to air. The hydroxide can therefore be used over and over again. The exposure to the air causes oxidation of the iron sulphide, and formation of sulphur. When the iron oxide contains 50 per cent. of sulphur, it is sold to the sulphuric acid manufacturers.

The chemical reactions taking place in the purifiers are—

(1) $Ca(OH)_2 + H_2S = CaS + 2H_2O$

(2) $Ca(OH)_2 + 2H_2S = Ca(SH)_2 + 2H_2O$
Calcium hydrosulphide

(3) $CaS + CS_2 = CaCS_3$
Calcium thiocarbonate

(4) $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$

(5) With iron oxide the main reaction is—

$$Fe_2O_3.3H_2O + 3H_2S = 2FeS + S + 6H_2O$$

On exposure to air the reaction is—

$$2FeS + 3O = Fe_2O_3 + 2S$$

The gas finally passes through the meter **M** to the gas holders. The tar and ammoniacal liquor are very valuable commercial products, and the working up of them into commercial substances is a great industry in itself.

One ton of good gas coal yields about 12,000 cubic feet of 16 candle power or 550 Therm gas, 1400 lb. of coke, 120 lb. of tar, and 20 gallons of ammoniacal liquor.

The following table shows the volume composition of a good coal gas of 17 candle power :—

	Per cent.	
Ethylene, acetylene benzene, etc.	5	Illuminants. Gases rich in carbon.
Marsh gas	35	Diluents. Non-illuminating but heat-giving gases.
Hydrogen	49	
Carbon monoxide	7	
Nitrogen	3	Impurities.
Carbon dioxide	1	
	100	

The causes of luminosity of flames were dealt with on page 64. The probable chemical changes which take place in the luminous flame are indicated below.

In the blue region **D**, Fig. 35, the hydrocarbons, marsh gas and ethylene, are partly burnt to water and partly converted into hydrogen and carbon monoxide.

$$CH_4 + O_2 = CO + H_2O + H_2$$
$$C_2H_4 + O_2 = 2CO + 2H_2$$

As the gases ascend the dark region **A**, they are partially converted by the heat of the burning material surrounding them into acetylene and hydrogen.

$$2CH_4 = C_2H_2 + 3H_2$$
$$C_2H_4 = C_2H_2 + H_2$$

In the luminous area **B**, complex changes take place, denser hydrocarbons and solid carbon being produced.

Finally, the carbon monoxide, hydrogen, and hydrocarbons, which escape combustion in the luminous area, burn in the non-luminous edge of the flame **C**.

HOMOLOGOUS SERIES OF HYDROCARBONS

Hydrocarbons are compounds of carbon and hydrogen. Great numbers of them are known. Methane, or marsh gas, is the first hydrocarbon of a series, the members of which can be arranged in order of their molecular weights. The difference in molecular weight between each member and the following member is always 14, corresponding to a difference of one atom of carbon and two atoms of hydrogen in the molecular formulæ of the hydrocarbons. Ethylene and acetylene are also the first members of series of hydrocarbons. Such series are known as *homologous series*.

The following table shows the names and formulæ of a few members of three series :—

Paraffin series	Olefine series	Acetylene series
Methane, CH_4	..	..
Ethane, C_2H_6	Ethylene, C_2H_4	Acetylene, C_2H_2
Propane, C_3H_8	Propylene, C_3H_6	Allylene, C_3H_4
Butane, C_4H_{10}	Butylene, C_4H_8	Crotonylene, C_4H_6
Pentane, C_5H_{12}	Amylene, C_5H_{10}	Valerylene, C_5H_8
General formula, CH_{2n+2}	General formula, C_nH_{2n}	General formula, C_nH_{2n-2}

The members of the same series show great similarity in both physical and chemical properties. The boiling-points, or melting-points, in the case of the higher members gradually increase with increasing molecular weight. Each hydrocarbon gives rise to a number of compounds, such as chlorides,

alcohols, ethers, aldehydes, acids, etc., so that there are similar series of each of these classes of compounds.

The chemistry of the compounds of carbon, exclusive of those dealt with in inorganic chemistry, is called *Organic Chemistry*. This name was originally given to the chemistry of those compounds which are found in organisms or are produced from organisms. It was believed that the compounds called *organic* could not be prepared in the laboratory from inorganic or " dead " materials, and that they could only be obtained through the agency of plants or animals, that is, of life. In 1828, however, Wöhler succeeded in obtaining from ammonium cyanate, which is undoubtedly inorganic, a compound called urea, which is undoubtedly organic. Since then thousands of organic compounds have been made in the laboratory from inorganic materials. Organic chemistry has developed to such an extent that the number of known carbon compounds probably greatly exceeds that of the known compounds of all the other elements. A few more of the common organic substances will now be studied in an elementary manner.

CHAPTER XXV

THE CARBOHYDRATES—STARCH, CELLULOSE, SUGARS

Exp. 160—To obtain starch from flour

Directions—Enclose a few grams of flour in a piece of muslin, calico, or linen (your handkerchief will do), and work it about for a few minutes under cold water contained in a porcelain dish. When the greater part of the flour has been worked through the calico, allow the milky liquid to settle and pour off the water from the sediment. Notice the tough, sticky character of the *gluten* left in the calico.

Exp. 161—To obtain starch from potatoes

Directions—Crush a small potato thoroughly, mix it well with water, decant off the milky liquid, and allow it to settle. Repeat the washing and decantation several times. Pour off the water from the sediment of starch.

Exp. 162—To determine some of the properties of starch

Directions—

(1) Examine a few grains of each of your specimens of starch under a powerful microscope. Draw the grains.

(2) Boil some water in a small beaker, and add to it about half a gram of starch. Notice the viscous, sticky character of the starch solution.

(3) To a few c.c. of cold starch solution add one or two drops of iodine solution. Next warm the solution until the blue colour just disappears. Finally, cool the solution.

(4) Warm a little starch solution with alkaline copper tartrate solution, *i.e.* with Fehling's solution.

(5) Heat a small quantity of dry starch in an evaporating dish in a hot air oven until it is converted into a yellowish compound, smelling like gum and soluble in water. This substance is called *dextrin* or *British gum*.

Exp. 163—To determine some of the properties of cellulose

Directions—

(1) Try the effect of chlorine, bromine, boiling dilute acids, and alkalis on pure cellulose (Swedish filter paper).

(2) Put strong caustic soda solution on a filter paper in a beaker. Gently warm.

(3) Dilute some strong sulphuric acid with half its volume of water and dip a filter paper into the solution. After a few seconds take out the filter paper. Wash and dry it.

(4) Precipitate copper sulphate solution with *cold* caustic soda solution; wash the precipitated copper hydroxide and dissolve it in the least possible quantity of strong ammonia solution. Put into the blue solution cotton wool or filter paper, and allow it to stand. When the cellulose has all dissolved, add acid. The cellulose should be thrown down as a gelatinous precipitate.

Exp. 164—To obtain solutions of maltose and glucose from starch

Directions—Maltose and glucose are sugars Make about 60 c.c. of a weak solution of starch and divide the solution into two parts.

To one part add a few c.c. of malt extract, or a little saliva, and warm to about 60° C.

To the second portion add a few drops of dilute sulphuric acid solution, and boil for some time.

Test a part of each solution for starch with iodine, and for sugars by warming gently with Fehling's solution. Maltose should be obtained in the first portion and glucose in the second portion. Both sugars give a yellowish-red precipitate of cuprous oxide with Fehling's solution.

Exp. 165—To examine and compare starch, cane sugar, glucose, and milk sugar

Directions—Carry out the following experiments with small quantities of each substance :—

(1) Taste it.
(2) Heat in an ignition tube.
(3) Warm with strong sulphuric acid.
(4) Boil with fairly strong caustic soda solution.
(5) Warm with Fehling's solution.
(6) Warm with ammoniacal silver nitrate solution.

Make the silver solution by adding dilute ammonia solution to silver nitrate solution until the precipitated silver oxide just redissolves. Then add *one drop* of caustic soda solution.

Tabulate your results.

Exp. 166—To hydrolyse cane sugar

Directions—Make a weak solution of cane sugar and boil it for some time with a few drops of dilute sulphuric acid.

Next make the solution alkaline and warm it with Fehling's solution. It will be found that the cane sugar has been converted into a substance or substances which reduce Fehling's solution to cuprous oxide.

STARCH $(C_6H_{10}O_5)_x$

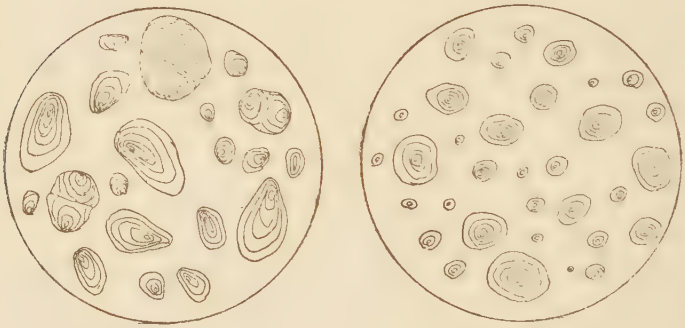
Occurrence—Starch is found chiefly in the seeds and tubers of plants. It serves as food for the young plant. Potatoes, wheat, rice, and maize are the chief sources of starch. Potatoes contain about 20 per cent., wheat about 50 per cent., and rice and maize about 80 per cent. of starch.

Formation—Starch is obtained by breaking up the grain or potatoes and washing the starch through fine sieves with water.

Properties—Starch is a white powder, insoluble in cold water, but soluble in hot water. The grains may be round, elliptical, or angular. They may vary considerably in size,

see Fig. 114. Under the microscope they appear to consist of concentric layers arranged round a nucleus. When warmed with water the grains swell up and burst, and form a semi-transparent solution which sets on cooling to a stiff paste. The insoluble cell walls, which make the starch paste turbid, are known as *starch cellulose.*

A solution of starch is coloured blue by iodine. The



Potato starch
Highly magnified

FIG. 114

Wheat starch
Highly magnified

colour disappears on warming, but reappears on cooling. This reaction forms a very delicate test for iodine.

When a solution of starch is warmed to 60° for some time with malt extract or saliva, the starch is converted into a sugar called maltose. This change is brought about by lifeless ferments called *enzymes.* The enzymes in extract of malt and in saliva are respectively *diastase* and *ptyalin.*

$$2(C_6H_{10}O_5)_x + xH_2O = xC_{12}H_{22}O_{11}$$ Maltose

When starch solution is warmed with dilute sulphuric acid, the starch is almost completely converted to glucose.

$$(C_6H_{10}O_5)_x + xH_2O = xC_6H_{12}O_6$$ Glucose

Maltose and glucose reduce Fehling's solution to cuprous oxide.

When dry starch is gently heated, it is converted to *dextrin* $(C_6H_{10}O_5)_x$. Dextrin is a yellowish powder which is soluble in water. It has a peculiar smell, and is known as *British gum.*

Starch is used for stiffening linen, sizing paper, and for the manufacture of British gum.

The value of x in the formulæ of starch and dextrin is not known.

CELLULOSE $(C_6H_{10}O_5)x$

Cellulose forms the framework of vegetable tissue. Cotton wool, cotton, linen, and paper are all fairly pure forms of cellulose. The mineral matter can be removed from them by soaking in hydrofluoric acid.

Properties—Cellulose is scarcely affected by boiling dilute acids, dilute alkalis, or the ordinary chemical reagents. Consequently, paper is much used for filtering.

Strong solutions of alkalis thicken and gelatinise the walls of cellulose fibre. A filter paper, treated with a strong solution of caustic soda, rapidly gelatinises, and shrinks down into the apex of the funnel supporting it. *Parchment paper* can be prepared by dipping filter paper for a second or two into sulphuric acid, diluted with half its volume of water, and drying and washing the paper. The undiluted acid rapidly dissolves cellulose.

A strong solution of copper oxide in ammoina will also dissolve cellulose. When acids are added to the solution, the cellulose is thrown down as a gelatinous precipitate. If paper is moistened with an ammoniacal solution of copper oxide and then dried, the surface fibres are gelatinised, and the paper is made impervious to water.

When pure cotton wool is treated, under proper conditions, with a mixture of fuming nitric acid and strong sulphuric acid, gun-cotton is produced. Gun-cotton has the composition $(C_{12}H_{14}O_4.(NO_3)_6)$, and may be regarded as *cellulose hexa-nitrate*. It is an excellent explosive.

CANE SUGAR (SUCROSE), $C_{12}H_{22}O_{11}$

Occurrence—Cane sugar occurs chiefly in the sugar cane and sugar beet. It occurs also to some extent in the flowers, roots, and sap of many plants and trees.

Manufacture—The sugar canes are cut up and squeezed between hot rollers. The expressed juice is boiled with milk of lime to convert organic acids and albuminoid substances into a scum, which can be skimmed off. The liquor is then concentrated to the crystallising point. The mother liquor,

which is drained away from the crystals, constitutes treacle or molasses. The raw sugar is refined by dissolving in water, boiling with lime, filtering, and passing the clear but brown liquid through vessels filled with animal charcoal. The brown colour is removed by the charcoal. Finally, the filtrate is concentrated until it crystallises.

Beet sugar is made from the sugarbeet, which containsabout 14 per cent. of cane sugar. The roots are cut into thin slices, and the sugar is washed out by water. The solution in water is treated in a way similar to that used for juice from the cane.

Properties—Cane sugar is a crystalline solid with a sweet taste. It has antiseptic properties. In candied fruits and in jams, sugar acts as a preservative. When heated above its melting-point, it turns brown and forms *caramel*, and when distilled, it gives off water, acetic acid, etc., and leaves a residue of sugar charcoal.

Boiled with dilute sulphuric acid, sugar is hydrolysed and converted into a mixture of glucose and fruit sugar.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fruit sugar}}{C_6H_{12}O_6}$$

A substance is said to be *hydrolysed* when it takes up the elements of water and splits into two different substances. When strong sulphuric acid is added to a few c.c. of a strong solution of sugar, the sugar is rapidly charred. The black product swells up enormously owing to inflation with steam, carbon dioxide, sulphur dioxide, and other gases.

Strong nitric acid oxidises cane sugar to oxalic acid (*q.v.*). Cane sugar will reduce Fehling's solution only on long boiling. It will not ferment with pure yeast, but it will ferment with brewer's yeast. In brewer's yeast is an enzyme, *invertase*, which has the power of converting cane sugar into a mixture of glucose and fruit sugar. These sugars then ferment with the yeast, forming alcohol and carbon dioxide.

Invertase fermentation—

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fruit sugar}}{C_6H_{12}O_6}$$

Yeast fermentation—

$$\underset{\text{Glucose and fruit sugar}}{C_6H_{12}O_6} = 2CO_2 + \underset{\text{Alcohol}}{2C_2H_6O}$$

GLUCOSE (*Dextrose* or *Grape Sugar*), $C_6H_{12}O_6$

Glucose occurs in grapes. It is manufactured by boiling starch with dilute sulphuric acid.

$$(C_6H_{10}O_5)_x + xH_2O = xC_6H_{12}O_6$$

The solution is neutralised with chalk, filtered, and decolorised with animal charcoal. The glucose is obtained on evaporation as a white amorphous mass.

Properties—It has a sweet taste. It turns caustic soda solution brown; it precipitates cuprous oxide from Fehling's solution; it reduces ammoniacal silver nitrate solution to silver. It ferments with yeast, giving alcohol and carbon dioxide.

Glucose is largely used in the manufacture of jam, and as a substitute for malt in brewing.

MILK SUGAR (*Lactose*), $C_{12}H_{22}O_{11}+H_2O$

This sugar is present in the milk of animals. Cow's milk contains about 5 per cent. of milk sugar.

Milk sugar is prepared from the liquid obtained by coagulating milk with rennet. When the mixture is filtered, and the filtrate evaporated, milk sugar is obtained is the form of hard crystals. The whey obtained in cheese-making is a source of milk sugar.

Properties—Milk sugar has a sweet taste. It turns caustic soda solution brown. It reduces Fehling's solution and ammoniacal silver nitrate solution. It does not ferment with ordinary yeast.

PRACTICAL EXERCISES

(1) Sterilise one-third of a test-tubeful of milk by putting the tube into boiling water for a quarter of an hour. Plug the mouth of the tube with cotton wool before sterilisation. Sterilise some more milk in a second tube, but do not plug with cotton wool. Into a third tube put some more milk and plug the mouth of the tube with cotton wool. Do not sterilise the milk in the third tube. Allow the three tubes to stand for some days. Then remove the cotton wool, smell the tube, and test the liquid with neutral litmus paper. Draw conclusions from the experiment.

(2) Try to prepare some milk sugar from milk.

CHAPTER XXVI

ALCOHOL—ETHER

Exp. 167—To obtain a specimen of alcohol from sugar

Directions—Make about 500 c.c. of a solution of grape sugar or cane sugar, and put it into a large flask. Add some

brewer's yeast. Connect the large flask to a small flask containing baryta water. See Fig. 115. Leave the apparatus for some days in a warm place.

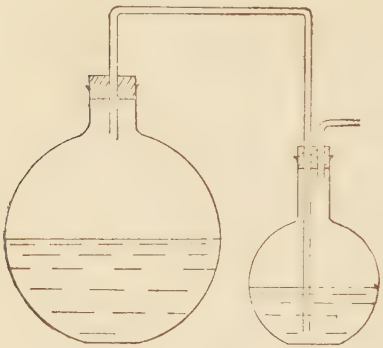


FIG. 115

Notice the formation of a white precipitate of barium carbonate in the small flask. What has caused the precipitate?

When gas is no longer evolved, filter from the yeast, and distil off about 100 c.c. of liquid. To the 100 c.c. of liquid add about 150 grams of quicklime, and allow the mixture to stand for a short time. Distil off about 20 c.c. of liquid from the mixture.

Test portions of the distillate for alcohol—

(1) by smell and taste,
(2) by applying a light
(3) by the iodoform test.

Iodoform test—Add a few crystals of iodine to 2 or 3 c.c. of alcohol. Next add caustic soda solution, drop by drop, shaking after each addition, until the colour of the iodine is just destroyed. Warm gently. The characteristic smell of iodoform will be noticed, and small yellow crystals of iodoform may separate out.

Exp. 168—To determine some of the properties of alcohol
Directions—

(1) Repeat the iodoform test of the last experiment, using larger quantities of the substances, and, after warming gently, allow the solution to stand for some time. Small yellow crystals of iodoform should fall.

(2) Heat alcohol with excess of strong sulphuric acid, and collect the evolved gas over water. Is the gas ethylene?

(3) Into a small distilling flask put about 40 c.c. of strong sulphuric acid, and about 60 c.c. of spirits of wine, a pure form of alcohol. Distil the liquid until about 20 c.c. of distillate has collected. Use a fairly long Liebig condenser. Do not bring a flame near the distillate.

Smell the distillate, pour a few drops on your hand. Bring a flame to a few c.c. of the liquid placed in a small basin. The distillate is ether mixed with some alcohol which has distilled over at the same time.

(4) Into a test-tube put a few drops of alcohol, add several c.c. of potassium bichromate solution acidified with dilute sulphuric acid, and warm the mixture. Note the smell of the substance formed, and the change of colour of the bichromate.

(5) To a few c.c. of spirits of wine, contained in an evaporating dish, add a piece of sodium about as large as a pea. Note the evolution of gas from the sodium. What is the gas? What happens to the sodium? Evaporate the liquid to dryness, and note the character of the residue.

ALCOHOL, C_2H_6O or C_2H_5OH

When yeast is added to a solution of cane sugar or grape sugar, fermentation sets in and the sugar is slowly converted to alcohol and carbon dioxide. The liquid, owing to the evolution of carbon dioxide, appears to boil; hence the name fermentation (Latin, *fermentum*, contraction of *fervimentum*, from *fervere* = *to boil*).

The yeast consists of spheroidal cells, which are composed of an interior of protoplasm enveloped by a wall of cellulose. Fermentation goes on only as the yeast grows. Buds are formed on the old cells. When the buds attain a certain size, they split off as separate cells. The temperature of the solution should be between 5° and 30° C., for beyond these limits the plant (yeast) stops growing, and consequently fermentation ceases. The best temperature is 25° C.

Before cane sugar can give alcohol, it must be converted into grape and fruit sugars by the action of the lifeless ferment, the enzyme *invertase*. The yeast then converts, first the grape sugar, and secondly the fruit sugar, into alcohol and carbon dioxide. Invertase is always present in brewer's yeast. The equations for the two fermentations are given on page 308. About 0.5 per cent. of the sugar is changed to succinic acid, and about 2.5 per cent. to glycerine. Traces of higher alcohols are also found. It is these alcohols which constitute *fusel oil*.

Beer is made from malt. Barley is steeped in water and allowed to germinate for a few days. During germination

the enzyme, *diastase*, is produced in the grain. Germination is stopped by heating the grain to about 100° C. The grain has now become *malt*. The malt is steeped in water at about 60° C., when the diastase converts the starch in the grain to maltose and dextrin. The liquid is then separated from the insoluble matter and boiled with hops, which act as a preservative, and impart a bitter flavour. The liquid is next allowed to stand at 25° C. with yeast, and glucose is added to provide additional alcohol. Finally, the fermented liquor is separated from the yeast and left to ripen in casks.

Diastatic fermentation—

$$\underset{\text{Starch}}{3(C_6H_{10}O_5)_x} + xH_2O = \underset{\text{Maltose}}{xC_{12}H_{22}O_{11}} + \underset{\text{Dextrin}}{xC_6H_{10}O_5}$$

Yeast fermentation—

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Alcohol}}{4C_2H_6O} + 4CO_2$$

Wines are made from grape juice. When the juice is allowed to stand, the grape sugar in the juice ferments, owing to the presence of ferment in the bloom on the outside of the grape.

Spirits are obtained from barley, molasses, malt, rye, potatoes, beet, and wine. Diastatic fermentation of barley is allowed to proceed longer than in the case of beer, in order that the dextrin may be converted into maltose. The fermented liquor from the yeast fermentation is distilled until the alcohol is removed. The alcohol is redistilled. Fusel oil is removed from the distillate by filtration through charcoal.

Brandy or cognac is the distillate from wine. Gin and whisky are the distillates from fermented barley. Rum is the distillate from fermented molasses. The differences in composition of these spirits are slight. The percentages of alcohol in fermented liquors are approximately—Brandy, whisky, and rum, 40 per cent.; gin, 35–40 per cent.; port, 20 per cent.; sherry, 17 per cent.; burgundy, 13 per cent.; hock, 8 per cent.; claret, 7 per cent.; strong ale, 6 per cent.; and lager beer, 3 per cent.

Alcohol, in the form of raw spirits, is manufactured from substances rich in starch by fermentation and subsequent distillation of the fermented liquor. Spirits of wine or rectified spirit, containing about 96 per cent. of alcohol, is obtained by

fractional distillation of the fermented liquor. By distillation of spirits of wine over quicklime, *absolute alcohol* (containing less than .5 per cent. of water) can be obtained.

Properties of alcohol—Pure alcohol is a colourless liquid, which has a burning taste and pleasant smell. It boils at 78° C. and freezes at −130° C. It mixes in all proportions with water and ether. It burns, forming carbon dioxide and water,

$$C_2H_6O + 3O_2 = 2CO_2 + 3H_2O$$

Towards acids it acts like a base, forming salts and water. Thus, when it is warmed with strong sulphuric acid, it forms ethyl hydrogen sulphate,

$$C_2H_5.OH + H_2SO_4 = C_2H_5.HSO_4 + H_2O$$

When heated with strong hydrochloric acid under pressure, it is partly converted to ethyl chloride.

$$C_2H_5OH + HCl = C_2H_5Cl + H_2O$$

That alcohol contains the group OH is shown by these reactions and also by its action with phosphorus pentachloride (*q.v.*).

$$C_2H_5.OH + PCl_5 = C_2H_5Cl + POCl_3 + HCl$$

Sodium reacts with alcohol and replaces a hydrogen atom. This action also indicates the presence of the group OH.

$$2C_2H_5OH + 2Na = 2C_2H_5ONa + H_2$$

Sodium ethylate

When heated with excess of strong sulphuric acid, alcohol gives ethylene; if excess of alcohol is used, ether is produced. Thus—

$$C_2H_5OH + H_2SO_4 = C_2H_5.HSO_4 + H_2O$$

$$C_2H_5.HSO_4 = C_2H_4 + H_2SO_4$$

Ethylene

$$C_2H_5.HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4$$

Ether

When heated with bleaching powder and water, alcohol forms chloroform, $CHCl_3$. With iodine and caustic soda, alcohol forms iodoform, CHI_3. When oxidised with a mixture of potassium bichromate and dilute sulphuric acid, alcohol forms aldehyde, a substance with a characteristic smell.

$$C_2H_6O + O = C_2H_4O + H_2O$$

Aldehyde

Alcohol, when taken into the body as a drink, actually lowers the temperature of the body about .2° C., while producing a sensation of warmth.

Methylated spirit consists of about 90 per cent. of raw spirits and about 10 per cent. of wood spirit, together with a small quantity of paraffin oil to make it unfit for drinking.

Alcohol is used largely as a solvent for scents, and for making the solutions of substances in alcohol known as *tinctures*.

ETHYL ETHER (*Ordinary Ether*), $(C_2H_5)_2O$

Ether is prepared from alcohol by warming it to about 140° C. with two-thirds of its volume of strong sulphuric acid. The apparatus used is shown in Fig. 116.

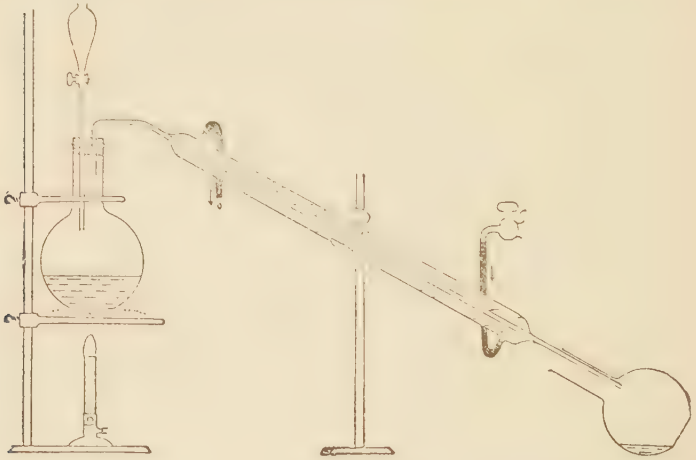


FIG. 116

To replace the liquids used up, a mixture of two parts of alcohol and one part of strong sulphuric acid is allowed to trickle slowly from the dropping funnel. In this way the process is made continuous. Ether collects in the flask.

$$C_2H_5OH + H_2SO_4 = C_2H_5.HSO_4 + H_2O$$
$$C_2H_5HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4$$

Properties—Ether is a very volatile, mobile liquid, which has a pleasant smell. It boils at 35° C. It is very inflammable, and its vapour forms an explosive mixture with air or oxygen.

$$(C_2H_5)_2O + 6O_2 = 4CO_2 + 5H_2O$$

Ether is only slightly soluble in water.

It is not a very active substance chemically. It is not attacked by sodium, caustic alkalis, weak acids, or phosphorus pentachloride in the cold.

If some ether is put into a beaker, placed on a few drops of water on a block of wood, and a rapid current of air is blown through the ether, evaporation takes place very rapidly, and so much heat is taken from the water that the latter freezes and fixes the beaker firmly to the wood.

Ether mixed with alcohol and chloroform (A. C. E. mixture) is used as an anæsthetic.

Ether is an excellent solvent for many fats, resins, oils, etc., and is frequently used to extract substances from solution in water, *e.g.* iodine and aniline.

CHAPTER XXVII

COMMON VEGETABLE ACIDS

Exp. 169—To prepare a solution of acetic acid from alcohol

Directions—Fit a flask of about 500 c.c. capacity with a cork and upright condenser, Fig. 117. Into the flask put about 30 grams of potassium bichromate, cover the crystals with dilute sulphuric acid (one of acid to four of water), and add about 20 c.c of alcohol. Boil gently for half an hour.

Next, fit up the condenser in the ordinary position, distil the liquid, and collect the portion boiling between 110° and 120° C.

Notice the smell of the distillate, and test the distillate with litmus and calcium carbonate.

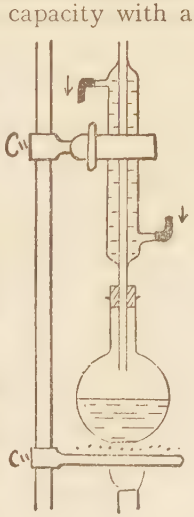


FIG. 117

Exp. 170—To prepare strong acetic acid from an acetate

Directions—Distil sodium acetate or calcium acetate with strong sulphuric acid, and collect the distillate.

(1) Test, as in the previous experiment, the acetic acid obtained.

(2) Find its boiling-point.

(3) Try to light some of the cold acid. Next, boil the acid, and try to light the vapour.

(4) Make sodium acetate from sodium carbonate, and lead acetate from lead carbonate or litharge.

Exp. 171—To determine the basicity of acetic acid

Directions—Weigh out into a 250 c.c. measuring flask about 2 c.c. of pure acetic acid. Fill up to the mark with distilled water, and mix thoroughly. Titrate the solution with standard caustic soda, using phenol phthalein as indicator.

The molecular weight of acetic acid is 60. Calculate the weight of caustic soda required to neutralise 60 grams of acetic acid, and so determine the number of molecules of caustic soda required to neutralise one molecule of the acid.

Exp. 172—To prepare oxalic acid from cane sugar

Directions—Into a large flask of about one litre capacity put 100 c.c of strong nitric acid. Warm on the water bath. Remove the flask to a draught chamber and add 25 grams of cane sugar. Great quantities of brown fumes of oxides of nitrogen are evolved. When the action has stopped, evaporate down the liquid on the water bath until it occupies about 25 c.c., and allow it to cool. If no oxalic acid crystallises out, evaporate still further.

Exp. 173—To find out some of the properties of oxalic acid

Directions—

(1) Heat some crystals of the acid with strong sulphuric acid and test the gases evolved.

(2) To a solution of oxalic acid add a few c.c. of dilute sulphuric acid. Warm gently, and add potassium permanganate solution drop by drop, until a permanent pink colour is obtained. Test the evolved gas for carbon dioxide.

(3) Find the basicity of the acid in a way similar to that used for acetic acid. The molecular weight of crystallised oxalic acid is 126.

(4) If the acid is found to be monobasic, make a specimen of its sodium salt. If it is found to be dibasic, make specimens of the acid and normal sodium salts.

Exp. 174—To find out some of the properties of tartaric acid

Directions—

(1) Find out if the crystals are soluble in water, and if they are acid to litmus. Taste a crystal.

(2) Try if the acid affects sodium carbonate (*a*) when the solids are mixed, and (*b*) when drops of water are added to the mixture.

(3) Heat one or two crystals of the acid with strong sulphuric acid.

(4) To a solution of tartaric acid add ammonia, and calcium chloride solution.

(5) To a strong solution of tartaric acid add a solution of a potassium salt and a few drops of acetic acid. Allow the solution to stand. Acid potassium tartrate should be precipitated in the form of small crystals.

(6) To a solution of tartaric acid add silver nitrate solution, and then very dilute ammonium hydroxide, until the precipitate formed is nearly redissolved. Gently warm. A silver mirror should be obtained.

ACETIC ACID, $C_2H_4O_2$ or $CH_3.COOH$

Acetic acid, in the form of vinegar, has long been known. It was first obtained pure in 1720 by Stahl.

Formation—(1) Acetic acid can be obtained by the oxidation of alcohol or aldehyde by means of a mixture of potassium bichromate and dilute sulphuric acid.

$$C_2H_5OH + O_2 = CH_3.COOH + H_2O$$

(2) Acetic acid is manufactured from the pyroligneous acid obtained in the distillation of wood. The liquid is neutralised with lime, and the wood spirit, water and acetone are distilled off. The residue of calcium acetate is gently heated to carbonise some of the tarry and resinous impurities, and is then distilled from copper vessels with the calculated quantity of strong hydrochloric acid.

$$(CH_3.COO)_2Ca + 2HCl = 2CH_3.COOH + CaCl_2$$

Calcium acetate

A distillate containing about 50 per cent. of acetic acid is obtained. This distillate is neutralised with caustic soda, the solution is evaporated to dryness, the residual salt is fused to

expel water, and the fused sodium salt is distilled with strong sulphuric acid. Pure *glacial acetic acid* distils over.

(3) Vinegar is obtained when weak wines, such as claret and hock, turn sour under the influence of the acetic acid ferment, *mycoderma aceti*. The oxygen required for this change is supplied by the air.

In the **French process** for the manufacture of vinegar, a small quantity of wine is placed in a large vat, covered with a perforated lid. The vat is previously soaked inside with hot vinegar. The ferment gets into the wine and grows in it until it covers the surface with a slimy film of the living ferment known as *mother of vinegar*. More wine is added at intervals until the vat is half full, when most of the vinegar is drawn off. More wine is then added, and the process is repeated.

The modern **German process** is often called the *quick vinegar process*. A large wooden vat, Fig. 118, with perforated sides, is fitted near the top and bottom with perforated discs, and the space between the discs is filled with beechwood shavings. The shavings are moistened with strong vinegar. They quickly become coated with the ferment. Weak alcohol, containing about 5 to 8 per cent. of spirit, and mixed with a small quantity of beer, vinegar, or malt extract to provide food for the ferment, is allowed to trickle slowly over the shavings. The temperature is kept as nearly as possible at 35° C., and the air supply is regulated. Too little air causes the formation of aldehyde; too much to the complete oxidation of the alcohol to carbon dioxide and water.

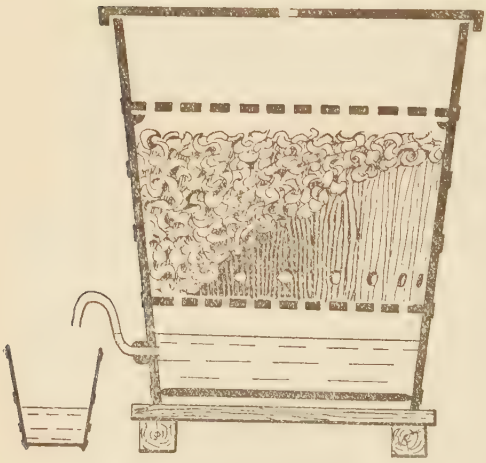


FIG. 118

The quickness of the process is due to the free supply of air, and to the large surface of ferment in contact with the liquid.

Properties—Acetic acid is a colourless liquid, which has a strong smell and a sharp, sour taste. It boils at 118° C. It solidifies at 16° C. to colourless crystals. It blisters the skin. The liquid will not burn, but the vapour burns to form carbon dioxide and water.

$$CH_3.COOH + 2O_2 = 2CO_2 + 2H_2O$$

It is a monobasic acid, only one of the four hydrogen atoms in its molecule being replacable by metals.

$$CH_3.COOH + NaOH = CH_3.COONa + H_2O$$

Sodium acetate

The other three hydrogen atoms are directly replaceable by chlorine, and three chlor-acetic acids can be obtained.

$$CH_3.COOH + Cl_2 = HCl + CH_2Cl.COOH$$

Mono-chlor-acetic acid

$$CH_2Cl.COOH + Cl_2 = HCl + CHCl_2.COOH$$

Di-chlor-acetic acid

$$CHCl_2.COOH + Cl_2 = HCl + CCl_3.COOH$$

Tri-chlor-acetic acid

It is obvious, therefore, that one hydrogen atom in acetic acid is combined differently from the other three.

The action of phosphorus pentachloride with the acid shows the presence of a hydroxyl group. Hydrochloric acid is given off from compounds treated with phosphorus pentachloride only when the compound contains the group OH.

$$CH_3.COOH + PCl_5 = POCl_3 + HCl + CH_3.COCl$$

Acetyl chloride

The common acids and oxidising agents have no action with acetic acid. The vapour density of the acid, at temperatures well above its boiling-point, corresponds to the formula $C_2H_4O_2$.

From these and other facts the formula $CH_3.COOH$ has been deduced for the acid. The hydrogen atom in the COOH group is the atom which is replaceable by metals.

Vinegar contains about 90 per cent. water, from 4 to 10 per cent. of acetic acid, some alcohol, colouring matters, sometimes potassium bitartrate, and phosphates.

All the normal acetates are soluble in water, but many of them are decomposed by boiling water. Thus, when

ferric acetate, $Fe(C_2H_3O_2)_3$, is boiled, basic ferric acetate, $Fe(C_2H_3O_2)(OH)_2$, is precipitated.

OXALIC ACID, $C_2H_2O_4$, or $\begin{matrix}COOH\\|\\COOH\end{matrix}$

This acid is found in combination in sorrel, rhubarb, and other plants as the acid potassium salt, or as calcium oxalate.

Formation—(1) The acid can readily be obtained in the laboratory by the oxidation of cane sugar. See page 316.

(2) Oxalic acid is made on the large scale from fine sawdust. This is fused with caustic soda, and the excess of alkali is washed out with water. The sodium salt, which is less soluble than the alkali is left; it is then dissolved in water, and converted into the insoluble calcium salt by the addition of lime. The calcium salt is decomposed with the calculated quantity of dilute sulphuric acid, and the oxalic acid solution is drawn off and evaporated to the crystallising point.

$$CaC_2O_4 + H_2SO_4 = CaSO_4 + H_2C_2O_4$$

Properties—Oxalic acid crystallises in long, colourless prisms, which contain two molecules of water of crystallisation. It is poisonous. It is a dibasic acid, and it forms two well-defined series of salts, acid and normal, *e.g.* $KHC_2O_4.H_2O$ and $K_2C_2O_4.H_2O$. Salts of sorrel or lemon, which may be used to remove iron-mould or ink stains, are composed of acid potassium oxalate combined with oxalic acid—

$$KHC_2O_4.H_2C_2O_4.2H_2O$$

When warmed with strong sulphuric acid, oxalic acid is split up into carbon monoxide and carbon dioxide.

$$C_2H_2O_4 = CO_2 + CO + H_2O$$

It is not affected by chlorine, hydrochloric acid, or nitric acid. The solution, when mixed with dilute sulphuric acid and warmed to about 60° C., is readily oxidised by potassium permanganate.

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 5H_2O$$

When the acid is heated to 100° C., the water of crystallisation is driven off. At higher temperatures the acid melts, partly sublimes, and partly breaks up into carbon dioxide and formic acid. The vapour density of oxalic acid cannot

be taken, but the molecular weight of the crystallised acid, determined by solution methods, is found to correspond to the formula $H_2C_2O_4.2H_2O$.

TARTARIC ACID, $H_6C_4O_6$, or

As the acid potassium salt and as the free acid, tartaric acid occurs widely in plants, *e.g.* in mountain ash berries, in grapes, and in many other fruits. Acid potassium tartrate is deposited during the fermentation of grape juice as a brown crystalline crust, called *tartar*. When the tartar is recrystallised, pure acid potassium tartrate or *cream of tartar* is obtained. The salt has, therefore, been known as long as wine has been made from grapes. Scheele, in 1769, first obtained the pure acid.

Formation—Tartaric acid is obtained from tartar. The salt is dissolved in water, and chalk is added until the solution is nearly neutralised. The precipitated calcium tartrate is filtered off, and the clear solution, which contains neutral potassium tartrate, is treated with calcium chloride solution. More calcium tartrate is thus obtained. The reactions may be represented by the equations—

$$2KHC_4H_4O_6 + CaCO_3 = CaC_4H_4O_6 + K_2C_4H_4O_6 + H_2O$$

Acid potassium tartrate — Calcium tartrate — Potassium tartrate

$$K_2C_4H_4O_6 + CaCl_2 = CaC_4H_4O_6 + 2KCl$$

The calcium tartrate is then decomposed with the calculated quantity of dilute sulphuric acid. The tartaric acid solution obtained is filtered from the insoluble calcium sulphate, and concentrated to the crystallising point.

Properties—Tartaric acid crystallises in large transparent crystals, which are readily soluble in water. When heated alone, it breaks up into a number of products. When heated with strong sulphuric acid, it blackens quickly, smells of burnt sugar, and gives off carbon monoxide. It readily reduces ammoniacal silver nitrate.

Only two of its six hydrogen atoms are replaceable by

metals. It is therefore a dibasic acid. It forms two series of salts. When a potassium salt is added to a strong solution of tartaric acid, acid potassium tartrate (cream of tartar) is slowly precipitated in small crystals. These crystals are insoluble in acetic acid. The normal potassium salt, $2K_2C_4H_4O_6 + H_2O$, is soluble in water.

Rochelle salt, $KNaC_4H_4O_6.4H_2O$, and tartar emetic, $2KSbO.C_4H_4O_6 + H_2O$, are useful soluble double tartrates, the latter salt being used as an emetic in medicine and as a mordant in calico printing. Fehling's solution is made by mixing solutions of copper sulphate and Rochelle salt, and making the mixture alkaline with caustic soda solution. The tartrate prevents the precipitation of the copper by the caustic soda.

Besides the tartaric acid (dextro-tartaric acid) just described, there are three more tartaric acids. All four acids have the formula $C_4H_6O_6$. They differ, however, in crystalline form, in solubility, and in their action towards polarised light. They can be accounted for theoretically by different arrangement of the atoms in the molecules.

PRACTICAL EXERCISES

Prepare specimens of potassium oxalate, potassium acetate, and sodium tartrate from oxalic acid, acetic acid, and tartaric acid respectively.

CHAPTER XXVIII

OILS—FATS—SOAPS—GLYCERINE—ORGANIC ANALYSIS

Exp. 175—To examine the action of fats and oils with alkalis

Directions—Try the effect of caustic soda solution on each of the substances—olive oil, linseed oil, paraffin oil, suet, lard, turpentine. Use a very small quantity of the substance, and warm it for some time with caustic soda solution. Shake well, notice if the fat or oil is dissolved, and if a lather is formed on shaking.

Exp. 176—To make soap from lard

Directions—Dissolve half a stick of caustic soda in about 50 c.c. of methylated spirit. Put a few grams of lard into an

evaporating basin on a water bath, cover the lard with the soda solution, warm and stir. When the lard has dissolved, continue to heat until all the alcohol is removed. Dissolve the residue in water.

To a small portion of the solution in water add hydrochloric acid and cool. What happens?

To the larger portion add strong salt solution; cool thoroughly, separate off the curd, press it into a little cake, and try if it will produce a lather.

Exp. 177—To observe the effect of a hard water on soap

Directions—Make a hard water by passing carbon dioxide into lime water until a clear solution is obtained. To this add a solution of soap, and shake. Filter off the curdy precipitate, wash it with water, remove it to a test-tube, and treat it with hydrochloric acid. Does any fat separate?

Exp. 178—To test for the presence of carbon and hydrogen in organic substances

Directions—With a large excess of pure granular copper oxide mix a small quantity of any one of the organic substances you have studied. Heat the mixture strongly in a hard glass tube, and pass the evolved gases through lime water. Notice the presence of any liquid on the cold part of the tube, and if any is present test it for water with white copper sulphate.

Evolution of carbon dioxide indicates the presence of carbon in the substance; formation of water indicates the presence of hydrogen.

Exp. 179—To test for the presence of nitrogen in organic substances

Directions—Into a test-tube put a piece of gelatine, horn, hair, or flesh, add a piece of sodium as large as a small pea, and heat strongly. Allow the tube to cool somewhat, and then break it into a small evaporating basin containing about 10 c.c. of water. Filter, and to the solution add ferrous sulphate solution, ferric chloride solution, and hydrochloric acid. A blue precipitate or a green coloration of Prussian blue indicates the presence of nitrogen in the substance.

OILS AND FATS

The term "oil" is in common use to denote three very different classes of compounds: first, the *true vegetable and animal oils* which are compounds of glycerine and acids, fats being the solid members of this group; second, the *mineral oils* of which petroleum is a representative; third, the *volatile or essential oils* of plants, which have characteristic and often delightful odours.

The true vegetable and animal oils are *esters* or salts of glycerol and certain organic acids, the so-called fatty acids; they are thus analogous to familiar inorganic compounds, namely *salts* of a weak base and an acid. Compare, for, instance, the action of caustic soda on ammonium sulphate—

Sodium hydroxide + ammonium sulphate → sodium sulphate + ammonium hydroxide

with its action on the principal fat in beef dripping

sodium hydroxide + glyceryl stearate (stearin) → sodium stearate (a hard soap) + glyceryl hydroxide (glycerol = glycerine)

Typical fats and oils of this group are olein or glyceryl oleate the main constituent of olive oil, palmitin or glyceryl palmitate in palm oil, glyceryl butyrate in butter. These glycerides of fatty acids are, to an enormous extent, used as food; but the lower grade fats and oils are converted into soap and glycerine by boiling with caustic soda, or, if soft soap is wanted, with caustic potash.

Some vegetable oils absorb oxygen from the air and pass on oxidation into translucent elastic solids. Such oils are called *drying oils*. The most important is linseed oil, but the oils from hemp-seed and sunflower-seed are also drying. Among semi-drying oils are cotton-seed, rape, and sesame. Non-drying oils include olive, almond and cod liver.

As a medium for paints and varnishes a drying oil is of course necessary, and linseed oil is best for these purposes. The "drying" property of linseed oil is used to form, with cork dust, a covering for floors, namely linoleum.

The mineral oils are hydrocarbons, mainly of the paraffin series. They are characterised by extreme stability, being unaffected by caustic soda, acids and the ordinary oxidising

agents. They are thus the most suitable oils for lubrication, but their chief uses are as fuel for internal combustion engines (petrol), for illumination (paraffin), and for firing boilers (impure heavy petroleum residues). The solid members of this series are well known as vaseline and paraffin wax.

The essential oils of plants are volatile and are usually obtained by distilling with steam the leaves, petals or rind (yellow orange rind gives good results in the laboratory). The essential oils are found floating on the surface of the distillate. They belong to no single chemical class, some being esters of various alcohols, some hydrocarbons, *e.g.* turpentine, hydrocarbons, but most mixtures of esters, hydrocarbons, and other classes of organic compounds. They are nearly all sweet-smelling, expensive, and used almost exclusively as perfume. Turpentine is a notable exception: it is comparatively cheap and is used in making paint, which it renders more fluid and quick-drying.

SOAPS

When a fat or a fatty oil is warmed with caustic soda solution, the glycerides of the fatty acids are converted into sodium salts, and glycerine is set free. This decomposition of fats and oils is called *saponification*. The term saponification was extended at one time to include the similar decomposition of ethereal salts by alkalis, but the term *hydrolysis* has now largely taken its place. In the case of the glyceride of palmitic acid the reaction is

$$\begin{array}{l} C_{15}H_{31}.CO.OCH_2 \quad NaOH \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad HO.CH_2 \\ \qquad\qquad\qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ C_{15}H_{31}.CO.OCH + NaOH = 3C_{15}H_{31}.COONa + HO.CH \\ \qquad\qquad\qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ C_{15}H_{31}.CO.OCH_2 \quad NaOH \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad HO.CH_2 \end{array}$$

Tripalmitin — Sodium palmitate — Glycerine

If strong salt solution is added to the solution obtained, the sodium salts separate out as a hard, white cake of soap.

Manufacture of soap—The fat is first rendered, *i.e.* melted and strained from the membrane or tissue. It is then mixed with caustic soda solution and heated with steam in iron pans until hydrolysis is complete, *i.e.* until all the fat is dissolved. On the addition of salt the sodium salts separate as a white granular mass which floats to the surface. The aqueous solution is drawn off and used for the manufacture of glycerine.

The soap, *i.e.* the mixture of sodium salts, is then again heated with a small quantity of caustic soda solution to ensure complete hydrolysis of the fat, and allowed to settle for two or three days. It is, finally, run into frames to cool and set.

Tallow (the fat from beef and mutton) and olive oil make the best hard soaps. Cheap soaps are made from palm oil, cotton-seed oil, coco-nut oil, and the waste fatty matter from many industries.

White curd soap is made from tallow; *Castile soap* is made from olive oil, and contains therefore a large proportion of sodium oleate; *lead soap*, used for diachylon plaster, is made from litharge and olive oil; *transparent soap* is made by dissolving yellow soaps, which contain some resin, in methylated spirit, driving off the alcohol, and allowing the liquid to set to a transparent mass; *soft soap* is made by boiling fats with caustic potash and allowing the solution to set to a jelly-like mass without the addition of salt.

The reaction of ordinary hard soaps with hard water produces insoluble calcium salts of the fatty acids of the soap. These calcium salts float on the water as a white curd. Until the whole of the calcium has been precipitated, a lather cannot be obtained with the water. The reaction in the case of sodium stearate and calcium sulphate is—

$$2C_{17}H_{35}.COONa + CaSO_4 = (C_{17}H_{35}COO)_2Ca + Na_2SO_4$$

Sodium stearate — Calcium stearate

BUTTER AND MARGARINE

Good butter, prepared from cream, contains about 90 per cent. of fat, 8 per cent. of water, and small quantities of curd, salt, casein, and milk sugar. The fat consists of the glycerides of stearic, palmitic, and oleic acids, together with about 7 per cent. of the glyceride of butyric acid and traces of other glycerides.

Margarine is prepared from the oils or fats of coco-nut, palm and cotton-seed. After purification these fats are hardened to the consistency of butter by *hydrogenation*, a process in which two atoms of hydrogen are added, in the presence of a catalyst, to the molecule of the glyceride constituting the fat. The processes vary and are trade secrets; finely divided nickel is one of the catalysts used. The hardened fat is then coloured, flavoured, and churned with milk to add vitamines—of which the chemically treated fat is destitute.

GLYCERINE OR GLYCEROL, $C_3H_5(OH)_3$

Glycerol is obtained largely from the aqueous solution left after the separation of the soap in the manufacture of the latter. The solution contains large quantities of sodium chloride, free alkali, and various fatty and resinous matters. The liquid is acidified, filtered from the fatty and resinous matter, neutralised, and evaporated down until the salts are deposited. The glycerine is obtained from the mother liquor by distillation with superheated steam. The distillate is evaporated to the required specific gravity, by means of steam heat, in pans from which the air is partly exhausted.

Glycerine is also manufactured by hydrolysis of tallow with dilute sulphuric acid or superheated steam.

Properties—Glycerine is a colourless, viscous liquid, which boils at 290° C. It readily absorbs water from the air. It has a sweet taste. It reacts with phosphorus pentachloride as if it contained three hydroxyl groups—

$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} + 3PCl_5 = \begin{array}{l} CH_2Cl \\ | \\ CHCl \\ | \\ CH_2Cl \end{array} + 3POCl_3 + 3HCl$$

It forms salts with hydrochloric, nitric, and sulphuric acids. The nitrate $C_3H_5(NO_3)_3$ is called *nitro-glycerine*. It is made by treating glycerine with a mixture of strong nitric and sulphuric acids under suitable conditions. It is a violent explosive. *Dynamite* consists of nitro-glycerine absorbed in kieselguhr a porous powder consisting of the remains of small siliceous marine animals. Dynamite is less liable to explode than nitro-glycerine, and is therefore safer to handle.

ORGANIC ANALYSIS

Tests for the presence of carbon, hydrogen, and nitrogen in organic compounds

When a compound containing carbon and hydrogen is heated with large excess of copper oxide, the carbon is oxidised to carbon dioxide, and the hydrogen to water. The copper oxide is reduced to metallic copper. Thus—

$$C_2H_2O_4 + CuO = 2CO_2 + H_2O + Cu$$

The carbon dioxide and water evolved can readily be

recognised by testing with lime water and anyhdrous copper sulphate respectively.

When an organic compound, containing nitrogen, is heated with metallic sodium, sodium cyanide is produced. If this cyanide is dissolved in water, and ferrous sulphate solution, ferric chloride solution, and hydrochloric acid solution are added, Prussian blue is obtained. Frequently the Prussian blue is formed in such small quantity that it appears as a green solution.

The reactions taking place in testing for nitrogen are the following :—

(1) The sodium forms sodium cyanide with the carbon and nitrogen present.

$$Na + C + N = NaCN$$

(2) The sodium cyanide forms sodium ferrocyanide with the ferrous sulphate.

$$FeSO_4 + 6NaCN = Na_4Fe(CN)_6 + Na_2SO_4$$

(3) The ferrocyanide reacts with the ferric chloride, forming Prussian blue.

$$3Na_4Fe(CN)_6 + 4FeCl_3 = Fe_7(CN)_{18} + 12NaCl$$

(4) The hydrochloric acid neutralises the caustic soda formed by the action of the excess of sodium with water, and allows the Prussian blue, which is decomposed by the caustic soda, to be formed and seen.

$$NaOH + HCl = NaCl + H_2O$$

Quantitative analysis of organic compounds

Estimation of carbon and hydrogen—The organic substance is weighed in a porcelain boat, and placed in a hard glass tube packed with granular copper oxide. The tube is heated strongly in a combustion furnace, and a slow stream of pure dry air or oxygen is passed through the tube. All the carbon is oxidised to carbon dioxide, and all the hydrogen to water. The carbon dioxide is absorbed in potash bulbs containing a strong solution of caustic potash, and the water is collected in a calcium chloride tube. The calcium chloride tube is connected to the potash bulbs with seamless india-rubber tubing. In this way the weights of carbon and hydrogen in the compound can be found. If nitrogen is present in the compound, a spiral of copper gauze, also strongly heated, is placed at the end of the tube. The heated copper breaks up

any oxides of nitrogen, which may have been formed, producing free nitrogen and copper oxide. The absorption of

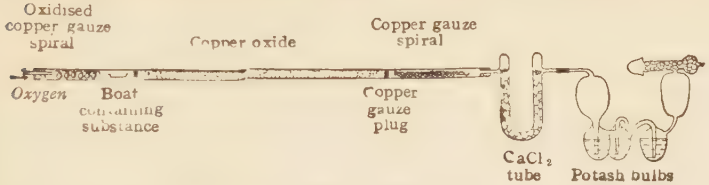


FIG. 119

the oxides of nitrogen in the potash bulbs is thus prevented. The tube is packed in the manner shown in Fig. 119.

Estimation of nitrogen—Nitrogen is estimated by heating the substance strongly with copper oxide, and collecting the nitrogen in a graduated tube over concentrated caustic soda solution. The combustion tube, Fig. 120, is first completely filled with carbon dioxide by heating magnesite. The copper oxide is next heated to redness, and the substance is very gradually heated until no more gas is evolved. Finally, the nitrogen in the tube is driven out by heating the magnesite again. A copper spiral is necessary to

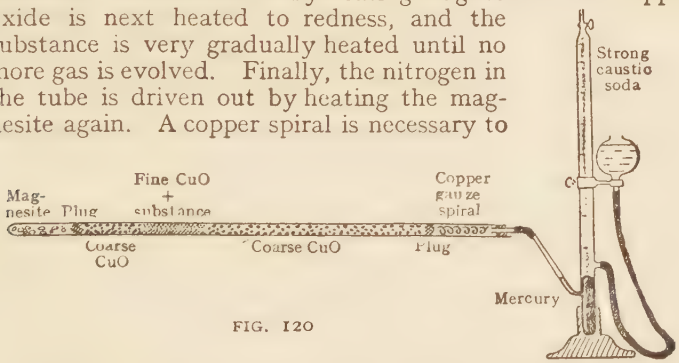


FIG. 120

split up the oxides of nitrogen formed. A packed tube and a collecting apparatus are shown in Fig. 120.

Oxygen cannot be directly estimated. The percentage of oxygen is obtained indirectly by estimation of the other elements.

PRACTICAL EXERCISES

(1) Prove the presence of carbon, hydrogen, and sodium in ordinary hard soap. For test for sodium, see p. 351.

(2) Test for carbon, hydrogen, and nitrogen in hair, wool, cotton, wheat, potato, etc.

CHAPTER XXIX

SILICA, GLASS, CLAY, AND POTTERY

SILICA

Si'lica (*silicon oxide*), SiO_2, occurs in a very pure form in nature as *opal*, *agate*, and *quartz* or *rock crystal*, and in less pure forms as *flint* and *sand*.

Formation—(1) Silica can be obtained by burning amorphous silicon in air or in oxygen. $Si + O_2 = SiO_2$

(2) It can be prepared by fusing sand or a natural silicate with about 4 times its weight of fusion mixture (a mixture of the carbonates of sodium and potassium in molecular proportions), extracting the cold mass with water, adding strong hydrochloric acid to the solution, and evaporating to dryness. The soluble chlorides in the residue are then extracted with water, and the silica collected in a filter and dried. The reaction of the acid with sodium silicate is—

$$Na_2SiO_3 + 2HCl = 2NaCl + H_2O + SiO_2$$

Properties—Silica in the form of quartz crystallises in hexagonal prisms terminated by hexagonal pyramids. The crystalline form is colourless when pure, is sufficiently hard to scratch glass, and it has a specific gravity of 2.6.

The amorphous silica prepared artificially is a white powder, which can be fused in the oxy-hydrogen flame to a glassy mass. This can be drawn into fine threads or formed into crucibles, dishes, etc. Silica ware is very infusible and is unaffected by all acids except hydrofluoric acid. It is attacked, however, by strong alkalis with which it forms silicates. It must, therefore, be regarded as an acidic oxide. The natural silicates are chiefly those of potassium, sodium, aluminium, calcium, and magnesium. The felspars, mica, serpentine, olivine, garnets, hornblende, augite, etc., are common rock-forming silicates.

When a mixture of sand with excess of powdered coke is heated in an electric furnace, *carborundum*, SiC, is formed.

$$SiO_2 + 3C = SiC + 2CO$$

Carborundum is a very hard crystalline solid used for grinding and polishing. It is usually black, but it is colourless when pure.

Silicon fluoride, SiF_4, can be obtained by burning silicon in fluorine or by dissolving silica in hydrofluoric acid.

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

It is prepared by warming gently, with strong sulphuric acid, a mixture of powdered fluorspar and sand.

$$SiO_2 + 2CaF_2 + 2H_2SO_4 = 2CaSO_4 + 2H_2O + SiF_4$$

Properties—Silicon fluoride is a colourless gas, which fumes in air owing to its action with the water vapour in the air. When the gas is passed into water it is decomposed with formation of hydrofluosilicic acid, H_2SiF_6, and gelatinous silicic acid, H_2SiO_3.

$$3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3$$

If the liquid is filtered, the hydrofluosilicic acid passes through in solution and the gelatinous silicic acid is left on the paper.

GLASS

The materials used for the manufacture of the different kinds of glass vary considerably, but one of them, silica, SiO_2, is present in all kinds. White sand is the form of silica used. Other ingredients are (1) sodium carbonate (free from iron), or sodium sulphate, or potassium carbonate ; (2) lime or calcium carbonate ; (3) red lead ; (4) cullet or broken glass ; (5) manganese dioxide.

(1) The object of the presence of the sodium carbonate, sodium sulphate, or potassium carbonate is the formation of an alkaline silicate with the sand. The presence of carbon helps the reaction.

$K_2CO_3 + 3SiO_2 = CO_2 + K_2O.3SiO_2$ Potassium silicate
$Na_2CO_3 + 3SiO_2 = CO_2 + Na_2O.3SiO_2$ Sodium silicate
$Na_2SO_4 + 3SiO_2 = SO_3 + Na_2O.3SiO_2$ „ „

(2) The lime (prepared from marble for the best glass) makes the glass tougher, harder, and less fusible. It forms calcium silicate with the sand.

(3) Red lead provides oxygen for the partial oxidation of iron, and tends to give brilliancy to the glass. It forms a silicate with the sand.

(4) The cullet acts as a flux, helps the reaction between the constituents of the new glass, and hinders loss of alkali by volatilisation.

(5) Manganese dioxide oxidises the iron from the green ferrous silicate to the slightly yellow ferric salt. It also forms a violet or pink manganese silicate, which helps to neutralise the green of the ferrous salt.

The finely ground materials are thoroughly mixed and then, with some cullet added, melted in a fire-clay pot. The scum, which collects on the surface of the molten mass, is skimmed off. The glass is then allowed to cool until pasty, when it is worked up into glass vessels of various kinds. The glass articles are annealed, *i.e.* very slowly cooled, by placing them in a long oven heated at one end and cold at the other, and by moving them very slowly along from the hot to the cold end. Annealing makes glass much less brittle, and prevents it from cracking as cooling proceeds.

Window or *crown glass* is a soda-lime glass. It is fairly hard and has a faint colour.

Bohemian glass is a silicate of lime and potash. It is used largely for chemical apparatus, owing to its resistance to the action of chemical reagents.

Common green glass or *bottle glass* is a silicate of lime and soda with some oxide of aluminium and iron oxide. It is to the latter oxide that it owes its green colour. It is readily attacked by acids.

Flint glass or *lead glass* is a potash-lead silicate. It has a high specific gravity; it is attacked readily by acids; it is easily fusible; it has a bright lustre and high refractive index. It is therefore suitable for making glass ornaments, the best table glass, lenses and other optical apparatus.

The composition of several different glasses is shown in the following table:—

Description of Glass	Silica	Potash	Soda	Lime	Magnesia	Lead Oxide	Alumina and Oxide of Iron
English window glass	70.71	—	13.25	13.38	—	—	1.92
Bohemian glass . .	73.13	11.49	3.07	10.43	0.26	—	0.89
Bottle glass . . .	65.57	2.72	4.86	20.42	—	—	6.15
English flint glass .	51.40	9.40	—	—	—	37.40	2.00

Glass may be coloured by the addition of various metallic oxides to the ordinary materials. Thus, *green* glass is obtained by addition of ferrous oxide, chromic oxide, or cupric oxide; *blue* glass by addition of cobalt oxide; *red* glass by addition of cuprous oxide, metallic copper, or metallic gold; *violet* glass by addition of manganese dioxide free from iron oxide; *orange* glass by addition of a mixture of ferric oxide and manganese dioxide; and *yellow* glass by the addition of sulphur or carbonaceous matter. The addition of cryolite or felspar or bone ash to the materials used for common glass produces the opaque *white*, *milk*, or *opal glass*. The enamel used for the lining of cooking vessels is a kind of glass made from sand, borax, soda, and white clay.

CLAY

Clay is a product of the weathering of rocks containing felspars, *e.g.*, granite, syenite, felspar porphyry, etc. It is a hydrated silicate of aluminium, and it possesses the property of forming a hard, stone-like mass when its water is driven off by heat.

The clay derived from a pure felspar is a white powdery mass of aluminium silicate from which nearly all the alkali has been washed away. It is called *kaolin* or *china clay*. In England it is obtained mainly from the granite formations of Devon and Cornwall. Its formation from a potash felspar may be represented by the equation—

$$\underset{\text{Felspar}}{K_2O.Al_2O_3.6SiO_2} + CO_2 + 2H_2O = \underset{\text{Clay}}{Al_2O_3.2SiO_2.2H_2O} + K_2CO_3 + 4SiO_2$$

The *common clays*, used for bricks, earthenware, and common pottery, contain varying amounts of iron oxide, and of lime and magnesia in the form of silicates, such as mica and undecomposed felspars.

Fire-clay is generally found under coal seams. It contains no alkalis. It was the old surface soil in which grew the plants forming the coal. These plants took up and made use of the alkalis in the soil. Fire-clay bricks and vessels stand very high temperatures without fusion.

The following table shows analyses of specimens of these three clays:—

	Kaolin	Brick-clay	Fire-clay
	Per cent.	Per cent.	Per cent.
Silica . . .	47.1	46.96	75.73
Alumina . . .	36.0	36.42	17.66
Ferric oxide . .	0.6	2.80	1.09
Lime	0.12	—	0.29
Magnesia . .	0.07	0.87	0.46
Alkalis . . .	3.13	0.91	—
Water . . .	12.9	12.04	5.0
Total . . .	99.92	100.00	100.23

POTTERY

In the manufacture of pottery the clay is mixed with water until the particles stick together and form a plastic mass, which is worked into the required shape on the potter's wheel. The vessel formed is slowly dried, and then baked at a definite temperature. It is glazed, if necessary, by dipping into a liquid glaze, drying, and once more baking.

Hard porcelain is made from a mixture of kaolin, quartz, and fe spar. The biscuit (*i.e.* porous) ware obtained by the first burning is glazed in a second burning at a high temperature with a glaze composed of felspar and lime. The glaze forms a glass, which fills the pores of the biscuit ware and produces semi-transparent porcelain or china. Berlin porcelain is a good example of this ware.

Soft porcelain is made from a mixture of kaolin, bone-ash, and felspar. It is burnt at a high temperature. The glaze, a lead-boric-acid glass, is fused on at a much lower temperature. This glaze does not penetrate as far as the glaze used for hard porcelain. Consequently soft porcelain is not as transparent as hard porcelain. Sèvres ware, Japanese ware, and English china are examples of soft porcelain.

Stoneware, of which the finest quality is *Wedgwood ware*, is made of less pure clay. It is burnt at a very high temperature, and glazed by throwing common salt into the kiln. The salt volatilises and reacts with the silicates of the stoneware, forming a glaze of double silicates of sodium and aluminium on the surface of the ware. Mineral-water bottles, glazed

pipes, paving tiles, and the grey stoneware decorated with blue and used for vases and drinking mugs, are samples of this ware.

Earthenware is not heated very strongly, and it is porous in the interior. It is made from clay mixed with ground flint and some Cornish stone. The latter is a partly weathered felspar, consisting of a mixture of kaolin, felspar, quartz, and mica. Earthenware is glazed in a second burning with an easily fusible mixture of clay, sand, soda, borax, and red lead.

Bricks are made from common clay which has been weathered for some months. The clay is screened from pebbles and mixed thoroughly with water, and with sufficient sand and powdered burnt clay (grog) to prevent undue shrinkage on burning. The bricks are then moulded, dried slowly in the air, and fired in kilns. A partial fusion takes place during the firing.

Fire-brick is made from fire-clay mixed with a large proportion of already burnt fire-clay or grog. The materials must be very carefully mixed in order to produce a brick which will withstand very high temperatures without fusion, and which will not crack when exposed to sudden changes of temperature.

CHAPTER XXX

METALS—ALLOYS—AMALGAMS—PREPARATION OF METALS—ACTION OF ACIDS ON METALS

Exp. 180—To find out some of the differences between metals and non-metals

Directions—Compare the metals iron, copper, lead, zinc, silver, with the non-metals oxygen, sulphur, bromine, phosphorus, carbon.

(1) Note, if possible, the lustre, and whether the element is transparent or opaque.

(2) Does the element exist in allotropic forms?

(3) Is the element malleable or brittle? Try.

(4) Does the element conduct electricity? Try by inter-

posing a piece of the element in an electric circuit containing an electric bell or galvanometer and a battery.

Exp. 181—To obtain mercury from mercuric oxide, and silver from silver nitrate by direct decomposition

Directions—

(1) Heat mercuric oxide in a hard-glass tube about six inches long until all the oxide is decomposed. The globules of mercury produced may be collected into a large globule by rubbing them with a glass rod. The mercury may be filtered from impurity by running it through a folded filter paper, perforated with pin-holes near the apex of the cone.

(2) Heat strongly one or two crystals of silver nitrate in a crucible with the blow-pipe flame. Metallic silver should be obtained.

Exp. 182—To obtain metals from their compounds by reduction with charcoal, etc.

Directions—

(1) Heat salts of silver, lead, bismuth, antimony, tin, and copper with the mouth blow-pipe, a small quantity of the salt being placed in a small hollow in a block of charcoal.

(2) If no metal is obtained in (1), mix the salt with about its own bulk of sodium carbonate, and heat on charcoal.

(3) If no metal is obtained in (1) and (2), mix the salt with a little powdered potassium cyanide (*a very powerful poison*), and again heat on charcoal.

You should be able to obtain specimens of all the metals mentioned in (1).

Exp. 183—To prepare metals from solutions of their salts by replacement with other metals

Directions—

(1) Place a strip of zinc in a solution of lead acetate, and leave it for some time. When the lead tree has stopped growing, test the solution for lead and for zinc. See Appendix.

$$(CH_3.COO)_2Pb + Zn = (CH_3.COO)_2Zn + Pb$$

Lead acetate — Zinc acetate

(2) Put a piece of sheet iron in a solution of copper sulphate. When the blue colour of the copper solution has disappeared, test the solution for copper and iron.

$$CuSO_4 + Fe = FeSO_4 + Cu$$

(3) Into a solution of stannous chloride put a strip of zinc foil and allow to stand. Take off the deposit of spongy tin from the zinc, wash it, and squeeze it into a ball in your fingers. Cut the ball with a knife, and note the lustre and colour of the tin. Test the solution for tin (stannous) and zinc.

$$SnCl_2 + Zn = ZnCl_2 + Sn$$

(4) Into a solution of silver nitrate put a piece of magnesium ribbon or a strip of zinc foil. When the crystals of silver have stopped growing, test the solution for silver, and for zinc or magnesium.

$$2AgNO_3 + Mg = Mg(NO_3)_2 + 2Ag$$

Exp. 184—To obtain copper by electrolysis of a solution of copper sulphate

Directions—Into a beaker put some copper sulphate solution, and pass an electric current through the liquid, using a platinum anode and a copper kathode. Notice that the solution gradually loses its colour as the copper is deposited on the kathode.

Exp. 185—To examine the action of acids on metals

Directions—

(1) Try the effect of dilute and strong hydrochloric acid, both hot and cold, on the common metals iron, lead, zinc, copper, and tin. Test the gases evolved. In the case of iron and tin, find out whether ferrous or ferric, stannous or stannic salts are produced. See Appendix.

(2) Study the action of dilute and strong nitric acid on the same metals. Find out if the white solid, obtained by the action of hot, strong nitric on tin, is a nitrate. See Appendix.

(3) Study the action of dilute and strong sulphuric acid on the same metals.

(4) Perform similar experiments with aqua regia (one part of strong nitric acid and three parts of strong hydrochloric acid).

Tabulate your results, and as far as possible name the products of reaction in every case.

METALS

The differences between metals and non-metals are both physical and chemical. Physical properties of common metals and non-metals you have compared for yourselves.

The general differences in the two classes of elements are summarised in the following table :—

METALS	NON-METALS
(1) Solids with high boiling-points.	(1) Gases, or solids with low boiling-points.
(2) Opaque.	(2) Many are transparent, but some are opaque.
(3) Do not exist in allotropic forms.	(3) Many exist in allotropic forms.
(4) Have a metallic lustre.	(4) When solid, often have a glassy lustre.
(5) Generally malleable and ductile.	(5) When solid, generally brittle
(6) Good conductors of heat and electricity.	(6) Bad conductors.
(7) Form basic oxides.	(7) Form acidic oxides.
(8) Form unstable hydrides or no hydrides.	(8) Form fairly stable hydrides.
(9) Form stable chlorides.	(9) Form chlorides, decomposed by heat or by water.
(10) Form amalgams with mercury.	(10) Do not form amalgams with mercury.

Exceptions may be found to nearly every one of these properties, but a general consideration of all will readily show whether an element is to be regarded as a metal or non-metal. Thus, many metals, *e.g.*, silver, gold, platinum, iron, can be precipitated as powders with no metallic lustre. Iodine and graphite have a metallic lustre. Chromium, a metal, forms an acidic oxide, CrO_3. Magnesium forms a chloride which can be decomposed by water. No one would hesitate, however, to class silver, gold, platinum, iron, chromium, or magnesium with the metals, or iodine and graphite with the non-metals.

ALLOYS

Many metals, when melted with other metals, mix thoroughly with the latter, and form *alloys*. It is often very

difficult to decide whether an alloy is a homogeneous mixture or a compound. The following method can be used to find out whether two metals form definite compounds with one another.

Suppose that an electric cell is constructed with a plate of platinum and a plate of a metal X, dipping into a suitable liquid. A definite electromotive force will be developed. If a plate of a more electropositive metal Y is fastened to the plate of X, the electromotive force of the cell will then be due to the more electropositive metal. This electromotive force will remain constant as long as any of the metal Y is undissolved. Let an alloy of X and Y be substituted for the plate of X. If any uncombined metal Y is present in the alloy, the electromotive force will be that due to this metal and the platinum. The electromotive force will remain constant until all the uncombined metal Y is dissolved, when it will suddenly fall to that due to X, or to an intermediate value due to a compound of X and Y. As soon as the fall in electromotive force occurs, the plate of alloy should be analysed. Its composition will be that of a compound of X and Y, if such a compound is present in the alloy. The compound Cu_3Sn was detected in this way.

Most alloys are found to be mixtures. Zn_3Hg, Al_3Mn, Cu_3Sn, Sn_4Pt, are examples of alloys of definite composition.

The following list shows the proportions of the metals present in a few of the common alloys :—

Brass varies from 90 per cent. copper and 10 per cent. zinc to 60 per cent. copper and 40 per cent. zinc.

Bronze coins contain 95 of copper, 4 of tin, and 1 of zinc. Other bronzes contain up to 16 per cent. of zinc.

Gun-metal varies from 91 of copper and 9 of tin to 84 of copper and 16 of tin.

Aluminium bronze contains 90 of aluminium and 10 of copper.

Pewter contains 80 of tin and 20 of lead.

Common solder consists of equal weights of tin and lead.

Type metal contains 70 of lead, 18 of antimony, 10 of tin, and 2 of copper.

German silver varies between the limits 50 to 70 per cent. copper, 20 to 40 per cent. zinc, 15 to 25 per cent. nickel.

Wood's metal, which melts below the boiling-point of water, consists of 4 of bismuth, 2 of lead, 1 of tin, and 1 of cadmium.

AMALGAMS

Many of the metals dissolve in mercury, giving a solution which is known as an *amalgam.* Sodium amalgam can readily be made by adding small pieces of sodium to warm mercury, which is covered with a layer of heavy paraffin oil. When it contains less than 1.5 per cent. of sodium, the amalgam is liquid ; when more than 1.5 per cent., it is solid.

Zinc plates for batteries are amalgamated on the surface by rubbing with mercury. Amalgamation largely prevents the solution of the zinc in the acid when the cell is not giving a current.

Tin amalgam is used for making mirrors, and amalgams of various metals are used as stoppings for teeth.

In an amalgam the metal is less active than in the pure form. Thus, sodium amalgam only reacts slowly with water, forming very small bubbles of hydrogen for some time, whereas the pure metal reacts very rapidly with water. Sodium amalgam is, therefore, very useful as a reducing agent.

GENERAL METHODS USED FOR THE PREPARATION OF METALS IN THE LABORATORY

(1) Strong heating of a compound of a metal

Some of the metals which are not oxidised by the air at high temperatures, can be obtained by strongly heating their compounds. Thus, compounds of silver, gold, and platinum, when strongly heated, give the metal—

$$2Ag_2O = 4Ag + O_2$$
Silver oxide

$$2Au_2O_3 = 4Au + 3O_2$$
Auric oxide

$$PtCl_4 = Pt + 2Cl_2$$
Platinic chloride

(2) Reduction of compounds of metals to the metallic state

Other metals can be obtained by reduction of their compounds with reducing agents, such as carbon, potassium cyanide, etc.

(*a*) With carbon alone. $Pb(NO_3)_2 = PbO + 2NO_2 + O$
$PbO + C = Pb + CO$

Beads of metallic silver can also be obtained in this way.

(*b*) With sodium carbonate and carbon.

The sodium carbonate fuses and converts the salt into carbonate, which, under the influence of heat, splits up to oxide and carbon dioxide. The oxide is then reduced by the carbon. Thus—

$$CuCl_2 + Na_2CO_3 = CuCO_3 + 2NaCl$$
$$CuCO_3 = CuO + CO_2$$
$$CuO + C = Cu + CO$$

Malleable beads of lead and silver, and brittle beads of antimony and bismuth can be obtained in this way. Copper is deposited as red scales.

(*c*) With potassium cyanide and carbon.

The potassium cyanide is a powerful reducing agent. It is converted into potassium cyanate by the oxygen of the metallic oxide, which is formed by heating the metallic salt.

$$SnO_2 + 2KCN = Sn + 2KCNO$$
Stannic oxide — Potassium cyanate

Copper can be obtained by this method much more readily than by (*b*).

(3) Replacement of a metal from a solution of one of its salts by means of a more electropositive metal

Only those metals which are not decomposed by water can be obtained in this way. The method therefore, could not be used for the production of sodium, potassium, barium calcium, etc. You have obtained a number of metals by this process. See page 336.

(4) Electrolysis of solutions of metallic salts

Silver, copper, gold, nickel can readily be obtained by electrolysis of solutions of their salts. The reaction taking place when copper sulphate solution is electrolysed between a platinum anode and copper kathode is probably—

$$2CuSO_4 + 2H_2O = 2Cu + \underbrace{2H_2SO_4}_{\text{At kathode}} + \underbrace{O_2}_{\text{At anode}}$$

METHODS USED FOR THE PREPARATION OF COMMON METALS ON THE LARGE SCALE

(1) Electrolysis of the fused hydroxide. Used for potassium and sodium.

$$2NaOH = \underbrace{2Na}_{\text{At kathode}} + \underbrace{H_2 + O_2}_{\text{At anode}}$$

(2) Electrolysis of the fused oxide. Used for aluminium.

$$2Al_2O_3 = \underset{\text{At kathode}}{4Al} + \underset{\text{At anode}}{3O_2}$$

(3) Reduction of the oxide by heating with carbon.

(*a*) When the metal is volatile, it is distilled off from the strongly heated mixture of metallic oxide and carbon. Used for zinc.

$$ZnO + C = Zn + CO$$

(*b*) When the metal is non-volatile, it is obtained in the molten state. Used for iron and tin.

$$Fe_2O_3 + 3C = 2Fe + 3CO$$
$$SnO_2 + 2C = Sn + 2CO$$

(4) Self-reduction. The natural sulphide is roasted until it is partly converted to oxide or to oxide and sulphate. The mixture of oxide and sulphide, or of oxide, sulphide, and sulphate, is then strongly heated. Used for lead and copper

$$\left.\begin{aligned} 2PbS + 3O_2 &= 2PbO + 2SO_2 \\ PbS + 2O_2 &= PbSO_4 \end{aligned}\right\} \text{Roasting}$$

$$\left.\begin{aligned} PbSO_4 + PbS &= 2Pb + 2SO_2 \\ 2PbO + PbS &= 3Pb + SO_2 \end{aligned}\right\} \text{Fusion}$$

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2 \quad \text{Roasting}$$
$$2Cu_2O + Cu_2S = 6Cu + SO_2 \quad \text{Fusion}$$

ACTION OF ACIDS ON METALS

Hydrochloric acid and the metals—*Dilute* hydrochloric acid in the cold dissolves magnesium, iron, and zinc, with evolution of hydrogen and formation of magnesium chloride, ferrous chloride, and zinc chloride respectively.

$$Fe + 2HCl = FeCl_2 + H_2 \qquad Zn + 2HCl = ZnCl_2 + H_2$$

Strong hydrochloric acid has the same action in the cold. When hot it will also dissolve tin and lead with evolution of

hydrogen and formation of stannous chloride and lead chloride respectively.

$$Sn + 2HCl = SnCl_2 + H_2 \qquad Pb + 2HCl = PbCl_2 + H_2$$

The action of the hot, strong acid with zinc and iron is the same as that of the cold dilute acid. Copper is attacked by hydrochloric acid only in presence of air. The action is very slow.

Nitric acid—*Dilute* nitric acid dissolves magnesium with evolution of hydrogen.

$$Mg + 2HNO_3 = Mg(NO_3)_2 + H_2$$

With other metals nitric acid gives little or no hydrogen, owing to the reaction of the nascent hydrogen with the acid. Oxides of nitrogen are therefore given off. Copper and zinc dissolve readily; iron dissolves fairly well, and forms a mixture of ferrous nitrate and ferric nitrate. *Strong* nitric acid reacts with iron, copper, zinc, lead, and tin. With iron, ferric nitrate is obtained; with tin, insoluble hydrated stannic oxide, $5SnO_2 + 5H_2O$, is formed.

The reactions of the acid, dilute or strong, cannot readily be represented by equations, for slight alterations of temperature and concentration of the acid, and the presence of nitrates in solution cause considerable alterations in the proportions of the oxides of nitrogen evolved. The following equations indicate the products that can be formed by the reduction of the acid by the nascent hydrogen produced:—

$$2HNO_3 + 2H = 2H_2O + 2NO_2$$
$$2HNO_3 + 4H = 3H_2O + NO_2 + NO$$
$$2HNO_3 + 6H = 4H_2O + 2NO$$
$$2HNO_3 + 8H = 5H_2O + N_2O$$
$$2HNO_3 + 10H = 6H_2O + N_2$$
$$2HNO_3 + 12H = 4H_2O + 2NH_2OH, \text{ Hydroxylamine}$$
$$2HNO_3 + 16H = 6H_2O + 2NH_3$$

The ammonia combines with nitric acid to form ammonium nitrate, NH_4NO_3. Pure strong nitric acid does not attack iron. A coating of the magnetic oxide of iron, Fe_3O_4, is supposed to be formed on the iron. This coat prevents further action of the acid with the metal. Iron in such a state is said to be *passive*. Passive iron does not possess the ordinary properties of iron. For example, it will not precipitate copper from copper sulphate solution.

Sulphuric acid—*Dilute* sulphuric acid dissolves iron, zinc, and magnesium with evolution of hydrogen and formation of ferrous sulphate, zinc sulphate, and magnesium sulphate respectively.

$$Fe + H_2SO_4 = FeSO_4 + H_2$$

Strong sulphuric acid does not attack the common metals in the cold. When hot, strong sulphuric acid is used, sulphur dioxide is evolved, and the sulphate of the metal is obtained The nascent hydrogen, formed in the first instance by the interaction of the metal and acid, reduces the strong sulphuric acid to sulphur dioxide. No hydrogen escapes. Thus, the reaction with zinc may be expressed by the two equations—

$$Zn + H_2SO_4 = ZnSO_4 + 2H$$
$$H_2SO_4 + 2H = 2H_2O + SO_2$$

Aqua regia—Aqua regia is a mixture of three parts of strong hydrochloric acid with one part of strong nitric acid. When it is heated the hydrochloric acid is oxidised by the nitric acid with formation of chlorine and nitrosyl chloride, NOCl.

$$3HCl + HNO_3 = 2H_2O + NOCl + Cl_2$$

It is the chlorine which gives to aqua regia its great solvent power. All the common metals, and even gold and platinum, are dissolved by it. The higher chloride of the metal, when more than one chloride exists, is formed.

$$Pt + 2Cl_2 = PtCl_4$$ Platinic chloride

In the case of lead, the chloride $PbCl_2$ is formed, although a higher chloride, lead tetrachloride, $PbCl_4$, exists. Lead tetrachloride is only stable at low temperatures.

CHAPTER XXXI

SODIUM AND ITS COMMON COMPOUNDS

Exp. 186—To find out some of the properties of sodium

Directions—**Caution**—*Do not touch sodium with wet fingers.*

(1) Cut a piece of sodium with a knife, and notice its softness, malleability, lustre, and the readiness with which it is oxidised.

(2) Put a small piece of sodium on water in a dish, try to

light the gas given off, and test some of the solution with litmus. Evaporate the remainder of the solution to dryness, and examine the residue. What is it?

(3) Try to burn sodium in the air. Use an iron spoon for the experiment. Dissolve the residue in water, test it with litmus, evaporate the solution to dryness, and compare the residue with that formed in (2).

Exp. 187—To make caustic soda from sodium carbonate

Directions—Make about 100 c.c. of a ten per cent. solution of sodium carbonate, and add about 20 grams of powdered slaked lime. Heat nearly to boiling-point for some minutes, until a drop of the clear liquid does not effervesce with acids. Filter, and evaporate the solution to dryness.

Examine the action of the residue with acids and solutions of salts.

Expose a little of the residue to air for some time. Does it behave like caustic soda?

Exercises—Make from sodium carbonate or caustic soda specimens of the salts—(1) Sodium sulphate, Na_2SO_4; (2) Acid sodium sulphate, $NaHSO_4$; (3) Sodium nitrate, $NaNO_3$; (4) Sodium bicarbonate, $NaHCO_3$.

SODIUM, Na

History—Sodium was discovered by Sir Humphrey Davy. He obtained it in 1807 by electrolysis of caustic soda.

Occurrence—As the chloride, sodium occurs in large quantities in sea water and in rock salt. It is also found as nitrate, *Chili saltpetre*, in Chili and Peru.

Formation—Sodium is manufactured by electrolysis of fused caustic soda. The hydrogen formed with the sodium at the kathode prevents the oxidation of the metal by the air.

$$2NaOH = \underbrace{2Na + H_2}_{\text{At kathode}} + \underbrace{O_2}_{\text{At anode}}$$

Properties—

Atomic weight = 23. Molecular weight = 23. Melting-point = 97° C.

Sodium is a soft white metal, easily oxidised by the air. Its specific gravity is less than that of water. When allowed to stand in air, sodium is oxidised to the oxide Na_2O, which then takes up water, forming sodium hydroxide, which again takes up enough water to dissolve it. If the solution is

allowed to stand for a long time, it absorbs carbon dioxide, so that the final product of the exposure of sodium to air is sodium carbonate.

With water sodium reacts, forming hydrogen and caustic soda.

$$2Na + 2H_2O = 2NaOH + H_2$$

Burnt in air, sodium forms a mixture of the two oxides Na_2O and Na_2O_2. Burnt in chlorine, it forms common salt, NaCl. The vapour density of sodium is 12.7, corresponding to a monatomic molecule Na. The vapour of sodium is violet in colour.

Sodium Monoxide, Na_2O—This is a basic oxide, made by heating sodium in nearly dry air to a temperature not above 180° C.

It is a greyish-white solid which dissolves in water, forming caustic soda.

$$Na_2O + H_2O = 2NaOH$$

Sodium peroxide, Na_2O_2—The peroxide is made by allowing sodium to burn brightly in oxygen.

$$2Na + O_2 = Na_2O_2$$

It is a yellowish-white solid, which is decomposed by warm water.

$$2Na_2O_2 + 2H_2O = 4NaOH + O_2$$

If it is added to well-cooled dilute hydrochloric acid, a solution of hydrogen peroxide is produced. The solution obtained is used for bleaching straw.

$$Na_2O_2 + 2HCl = 2NaCl + H_2O_2$$

Sodium peroxide is a powerful oxidising agent. Carbonaceous substances, in contact with it, ignite spontaneously; for example, sugar ground up in a mortar with sodium peroxide is ignited.

Sodium hydroxide (*caustic soda*), **NaOH**—Sodium hydroxide is readily obtained by warming a weak solution of sodium carbonate with slaked lime, until the clear liquid no longer effervesces with acids. The precipitated calcium carbonate is filtered off, and the solution is evaporated to dryness.

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH$$

The solution of carbonate must be dilute or the caustic soda solution will attack the calcium carbonate, and produce once again sodium carbonate and calcium hydroxide.

Caustic soda is prepared commercially by the above method

and also by several electrolytic processes. One of the most interesting of the latter is the Hargreaves-Bird process. The cell used is shown in Fig. 121.

A solution of salt is electrolysed in a cell the walls of which consist of asbestos impregnated with sodium silicate. The anode is of carbon and the kathode is a network of copper surrounding the outside of the asbestos cell walls. The asbestos cell is surrounded by an outer cell through which

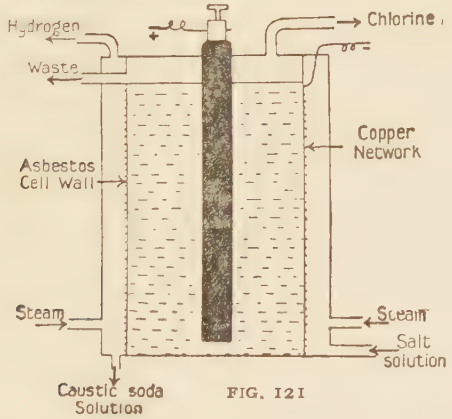


FIG. 121

steam can be blown. Chlorine escapes from the asbestos cell, the sodium ions pass through the asbestos walls and react with the steam in the outer cell forming hydrogen and caustic soda solution.

$$2NaCl = 2Na + Cl_2$$
$$2Na + 2H_2O = 2NaOH + H_2$$

Properties—Caustic soda is a white, strongly caustic solid, which deliquesces in air. It dissolves in water with evolution of heat. It is strongly alkaline, neutralises acids, absorbs carbon dioxide, and on warming liberates ammonia from ammonium salts.

$$NH_4Cl + NaOH = NaCl + NH_3 + H_2O$$

It is used in large quantities for soap-making.

Sodium chloride (*common salt*), **NaCl**—Salt is mainly obtained from deposits of rock salt. These deposits are either mined in the ordinary way, or a boring is made, water

is pumped down and allowed to dissolve salt, and the brine so obtained is pumped up and evaporated.

On the shores of the Mediterranean Sea some salt is made by evaporation of sea water in large shallow basins by means of the sun's heat.

In the laboratory, sodium chloride may readily be made by neutralising sodium hydroxide or carbonate with hydrochloric acid.

$$NaOH + HCl = NaCl + H_2O$$

A pure salt is precipitated when a saturated solution of common salt is poured into twice its volume of strong hydrochloric acid. Salt is almost insoluble in strong hydrochloric acid.

Properties—Sodium chloride crystallises from water in small cubes. It is not deliquescent when pure. The deliquescence of common salt is caused by small impurities of calcium and magnesium chlorides.

Salt is a necessary article of food for man and animals. The hydrochloric acid in the gastric juices of the stomach is derived from it.

Sodium carbonate (*washing soda*), Na_2CO_3—Sodium carbonate is manufactured in large quantities. Nearly a million tons of it are made annually in Great Britain. The two processes in use are named after their discoverers, Leblanc and Solvay.

Leblanc process—(1) Common salt is heated with strong sulphuric acid until the whole of the salt is converted into sodium sulphate.

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$
$$NaHSO_4 + NaCl = Na_2SO_4 + HCl$$

The hydrochloric acid is not wasted. It is passed up high towers filled with coke, over which water is trickling, and the solution obtained is used commercially for the manufacture of chlorine, etc.

(2) The sodium sulphate, or "salt cake," is then mixed with limestone and coal slack, and heated strongly in a revolving furnace.

$$Na_2SO_4 + CaCO_3 + 2C = Na_2CO_3 + CaS + 2CO_2$$

The product, which consists mainly of sodium carbonate and calcium sulphide, is known as "black ash." The sodium carbonate is dissolved out in cold water, and the solution is

evaporated to the crystallising point. Crystals of washing soda, $Na_2CO_3.10H_2O$, are thus obtained.

Solvay process or *ammonia-soda process*—This process consists of saturating brine (*i.e.* saturated common salt solution) with ammonia, and forcing carbon dioxide under slight pressure through the solution. The reaction is represented by the equation—

$$NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl$$

The sodium hydrogen carbonate is much less soluble than ammonium chloride, and therefore crystallises out. The ammonium chloride is heated with lime, and the ammonia formed is used again.

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O$$

The lime is obtained by heating limestone in kilns.

$$CaCO_3 = CaO + CO_2$$

The carbon dioxide from the kilns is used for the formation of the carbonate. The sodium hydrogen carbonate is finally heated in order to convert it into normal sodium carbonate, and the carbon dioxide evolved is used in the first part of the process.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

Properties—Sodium carbonate crystallises in large transparent crystals, containing ten molecules of water of crystallisation. The crystals on exposure to air effloresce and crumble to a white powder, $Na_2CO_3.H_2O$. The solubility of sodium carbonate increases with rise of temperature to a maximum of 59 at 33° C., after which it gradually decreases to 45 at 100° C. The solution is alkaline to litmus. Sodium carbonate may be heated to redness without appreciable decomposition.

Sodium hydrogen carbonate or sodium bicarbonate, $NaHCO_3$—This salt can be obtained as a white precipitate by passing carbon dioxide into a saturated solution of the normal carbonate. It is less soluble than the normal salt.

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$$

When the dry bicarbonate or its solution is heated, carbon dioxide is given off and the normal carbonate is obtained.

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

Baking powder consists largely of sodium bicarbonate. The carbon dioxide evolved during the baking makes the cooked materials "light."

Sodium sulphate, Na_2SO_4—Sodium sulphate is readily made by neutralisation of sodium hydroxide or sodium carbonate with sulphuric acid, or by heating sodium chloride with strong sulphuric acid.

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2$$
$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

Properties—Sodium sulphate crystallises in large colourless prisms which have the composition $Na_2SO_4.10H_2O$ (Glauber's salt). When exposed to the air, the crystals effloresce and crumble to the anhydrous salt, Na_2SO_4. The solubility of the salt increases to a maximum at 34° C., and then decreases slowly with rise of temperature. At 34° C. the crystals of $Na_2SO_4.10H_2O$ melt in their water of crystallisation. The solution, evaporated at or above that temperature, deposits crystals of anhydrous sulphate. Above 34° C., therefore, a saturated solution of sodium sulphate is in contact with the solid, Na_2SO_4. The curve of solubility, shown in Fig. 4, represents, therefore, the solubility of the sulphate in contact with $Na_2SO_4.10H_2O$ up to 34° C., and above 34° C. the solubility of the sulphate in contact with Na_2SO_4.

Sodium sulphate may be heated to redness without decomposition. When heated on charcoal, it is reduced to sodium sulphide, Na_2S.

$$Na_2SO_4 + 4C = Na_2S + 4CO$$

Sodium hydrogen sulphate, $NaHSO_4$, is obtained by mixing equivalent quantities of solutions of sodium sulphate and sulphuric acid, and evaporating the mixture at a temperature above 50° C.

$$Na_2SO_4 + H_2SO_4 = 2NaHSO_4$$

The salt is strongly acid to litmus.

Sodium nitrate, $NaNO_3$, occurs in large quantities in Chili and Peru as Chili saltpetre. It can readily be prepared by neutralising nitric acid with sodium hydroxide or sodium carbonate.

$$NaOH + HNO_3 = NaNO_3 + H_2O$$

Properties—It is a crystalline salt. It deliquesces on exposure to air, and consequently cannot be used as a substitute for potassium nitrate in the manufacture of gunpowder. It is very soluble in water. When heated strongly, it gives off oxygen, nitrogen, and oxides of nitrogen. It is largely used as a manure, and for the manufacture of nitric acid.

Sodium thiosulphate, $Na_2S_2O_3$—This salt is the " hypo " of the photographer. It is made by exposing the " alkali waste " from the Leblanc process to the action of the air. The waste becomes charged with calcium thiosulphate, which is extracted with water and decomposed by the addition of sodium carbonate.

$$CaS_2O_3 + Na_2CO_3 = Na_2S_2O_3 + CaCO_3$$

It can be obtained also by boiling sodium sulphite solution with sulphur.

$$Na_2SO_3 + S = Na_2S_2O_3$$

The thiosulphate crystallises when the solution is concentrated.

Properties—The crystals have the composition—

$$Na_2S_2O_3 \cdot 5H_2O$$

With dilute acids sodium thiosulphate reacts, forming sulphur dioxide and a precipitate of sulphur.

$$Na_2S_2O_3 + 2HCl = 2NaCl + S + SO_2$$

It is used by the photographer for " fixing," that is for dissolving out the silver salts from plates and paper sensitised with silver chloride and bromide. When the silver salt is removed, light has no further action on the plate or paper. The reaction is—

$$AgCl + Na_2S_2O_3 = NaCl + NaAgS_2O_3$$

Soluble in water

Test for Sodium—If a platinum wire is moistened with strong hydrochloric acid, dipped into a powdered sodium salt, and held in a bunsen flame, an intense yellow coloration is given to the flame by the sodium salt.

CHAPTER XXXII

POTASSIUM AND ITS COMMON COMPOUNDS

Exp. 188—To find out some of the properties of potassium

Directions—**Caution—Do not touch potassium with wet fingers**

(1) Cut a piece of potassium with a knife, and notice its softness, malleability, lustre, and the readiness with which it is oxidised.

(2) Put a very small piece of potassium on water in a dish and notice all that happens. Test some of the solution with

litmus, evaporate the remainder to dryness, and examine the residue. What is the residue?

(3) Burn a small piece of potassium on an iron spoon in air, dissolve the residue in water, evaporate the solution to dryness, and compare the residue with that obtained in (2).

Exp. 189—To test for potassium in potassium salts

Directions—

(1) Moisten the salt with strong hydrochloric acid, dip into it a platinum wire, and heat the wire in the bunsen flame. If the yellow sodium flame hides the potassium flame, examine the flame through blue glass. The yellow light is cut off by the blue glass, but the lilac potassium flame is visible through the glass.

(2) To a strong solution of a potassium salt add a strong solution of tartaric acid. A white crystalline precipitate of potassium hydrogen tartrate forms slowly.

(3) Into a small dish put one or two c.c. of a solution of a potassium salt, add an equal volume of alcohol, and then a few drops of platinic chloride solution. On gently warming and stirring, a yellow precipitate of potassium chlor-platinate forms.

Exp. 190—To prepare potassium hydrogen carbonate from the normal carbonate

Directions—The acid carbonate is much less soluble in water than the normal salt. Make a strong solution of the normal salt, cool the solution, and pass into it carbon dioxide until a considerable quantity of the acid carbonate has crystallised out. Filter, and wash the acid carbonate on the filter with small quantities of *cold* water. Dry the salt by pressing between filter papers. It is decomposed by heat.

Exercises—

(1) From potassium carbonate prepare specimens of the sulphate, chloride, and nitrate.

(2) From the normal carbonate prepare a specimen of the hydroxide in a similar way to that used for the preparation of caustic soda. See Exp. 187.

POTASSIUM, K=39

Potassium occurs in nature as the chloride in *sylvine*, KCl, as a double chloride of potassium and magnesium in *carnallite*, $KCl.MgCl_26H_2O$, and as the nitrate as an incrustation on the

soil in some parts of Chili and Peru. The ashes of land plants also contain potassium in the form of carbonate.

Formation—Metallic potassium was first obtained in 1807 by Sir Humphrey Davy by the electrolysis of moist caustic potash. It is now manufactured by electrolysis of fused caustic potash. The hydrogen formed with the potassium at the negative pole prevents the oxidation of the metal by the air. Compare sodium.

$$2KOH = \underbrace{2K}_{\text{Kathode}} + \underbrace{H_2 + O_2}_{\text{Anode}}$$

Properties—Atomic weight = 39. Molecular weight = 39. Melting-point = 62° C. Specific gravity = .87.

Potassium is a soft white metal, which tarnishes rapidly in air. When allowed to stand in air, it first takes up oxygen, forming the oxide K_2O, which takes up water and carbon dioxide from the air, forming first hydroxide and then carbonate.

With water potassium reacts more vigorously than sodium, forming caustic potash and hydrogen. Sufficient heat is produced to light the hydrogen, which burns with a flame, coloured lilac by the potassium.

$$2K + 2H_2O = 2KOH + H_2$$

Potassium burns in air, forming a mixture of the oxides K_2O and K_2O_4. Burnt in chlorine, it forms potassium chloride, KCl, and when heated in carbon dioxide it burns, forming potassium carbonate and carbon. The vapour density of potassium is 18.8, corresponding to a monatomic molecule, K. Its vapour is violet-blue in colour.

Potassium peroxide, K_2O_4, may be obtained by heating potassium in excess of oxygen. It is a yellow powder, which splits into potassium monoxide on heating. With water it reacts, forming caustic potash, hydrogen peroxide, and oxygen.

$$K_2O_4 + 2H_2O = 2KOH + H_2O_2 + O_2$$

Potassium monoxide, K_2O, is obtained by heating the peroxide. It is obtained as a grey brittle mass, which is very deliquescent, and which combines with water with incandescence, forming caustic potash.

$$K_2O + H_2O = 2KOH$$

Potassium hydroxide (*caustic potash*), **KOH**, is prepared by warming a dilute solution of potassium carbonate with

slaked lime, until the clear liquid no longer effervesces with acid. The precipitated calcium carbonate is filtered off and the solution is evaporated to dryness.

$$K_2CO_3 + Ca(OH)_2 = CaCO_3 + 2KOH$$

The solution of carbonate must be dilute in order to prevent the caustic potash from attacking the calcium carbonate.

Properties—Caustic potash is extremely like caustic soda in its properties. Like it, it is a white caustic solid, which is deliquescent, soluble in water with evolution of much heat, and strongly alkaline. It liberates ammonia from ammonium salts in a similar way.

Potassium chloride, KCl—This salt is prepared by dissolving potassium carbonate in dilute hydrochloric acid, or by neutralising caustic potash with hydrochloric acid, and evaporating the solution until it crystallises on cooling. On the large scale it is obtained by re-crystallising *carnallite*. This double salt splits into its constituents in solution, and when the solution is concentrated, the less soluble potassium chloride crystallises first, leaving the magnesium chloride in solution.

Potassium chloride is extremely like sodium chloride in its properties.

Potassium carbonate, K_2CO_3—This salt was formerly obtained from the ashes of wood (pot-ashes). It is now made from the potassium chloride of the Stassfurt supplies by a process exactly similar to the Leblanc soda process. The pure carbonate can be made by heating cream of tartar or the acid carbonate. Thus—

$$2KHC_4H_4O_6 = K_2CO_3 + 3C + 4CO + 5H_2O$$
$$2KHCO_3 = K_2CO_3 + H_2O + CO_2$$

The anhydrous carbonate is a very deliquescent white powder. From solution in water the salt crystallises in prismatic needles of the composition $K_2CO_3.3H_2O$.

Potassium hydrogen carbonate (*bicarbonate*), **$KHCO_3$**, is prepared by passing carbon dioxide through a strong solution of the normal carbonate. The bicarbonate, which is much less soluble than the normal salt, crystallises out.

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3$$

If the dry bicarbonate or its solution is heated, carbon dioxide is given off and the normal carbonate is formed.

$$2KHCO_3 = K_2CO_3 + H_2O + CO_2$$

Potassium sulphate, K_2SO_4, is made by methods similar to those used for making sodium sulphate. Its crystals differ from those of sodium sulphate in containing no water of crystallisation. Its solubility is greater in hot than in cold water. The acid sulphate is very soluble and is strongly acid to litmus.

Potassium nitrate (*nitre, saltpetre*), KNO_3, occurs as an incrustation on the soil in hot countries. This nitre is produced through the agency of certain bacteria, which, in presence of potashes and other bases, convert decaying nitrogenous matter into nitre and other nitrates. In Europe nitre is made artificially by mixing animal refuse with garden soil and slaked lime, protecting the heaps from rain, exposing them to the air, and watering them from time to time with drainage from manure. The calcium nitrate produced is extracted with water, and the solution is mixed with potassium carbonate. Calcium carbonate is precipitated and nitre remains in solution.

$$Ca(NO_3)_2 + K_2CO_3 = 2KNO_3 + CaCO_3$$

Nitre can be prepared in the laboratory by the general methods used for the preparation of salts.

Properties—Nitre crystallises from solution in long rhombic prisms, which contain no water of crystallisation, and which are not deliquescent. Its solubility increases rapidly with rise of temperature. Its solubility at 0° C. is 13.3, and at 100° C. it is 247. It melts at 339° C. Heated more strongly, it loses oxygen and forms the nitrite.

$$2KNO_3 = 2KNO_2 + O_2$$

It is, therefore, a powerful oxidising agent at high temperatures. A small piece of charcoal or sulphur, thrown on molten nitre, takes fire and burns vigorously.

$$4KNO_3 + 5C = 2K_2CO_3 + 2N_2 + 3CO_2$$
$$2KNO_3 + 2S = K_2SO_4 + SO_2 + N_2$$

Nitre is used largely in the manufacture of gunpowder, matches, and fireworks. Gunpowder consists roughly of 75 parts of nitre, 15 of charcoal, and 10 of sulphur. The nitre provides the oxygen for the rapid combustion of the sulphur and charcoal.

Tests for potassium—

(1) The potassium flame coloration is lilac. It is visible through blue glass.

(2) If a strong solution of tartaric acid is added to a strong solution of a potassium salt, a white crystalline precipitate of potassium hydrogen tartrate forms slowly.

(3) The platinic chloride test (see Exp. 189) depends on the reaction :—

$$2KCl + PtCl_4 = K_2PtCl_6$$

Potassium chlor-platinate.

Similarity of potassium and sodium—Potassium and sodium are put into the same sub-group of the Periodic Classification. We should, therefore, expect the metals and their compounds to be very similar. This is the case. Both metals are soft and easily oxidised by the air ; both are lighter than water ; both decompose water at ordinary temperatures, forming very strong bases and setting free hydrogen.

Their oxides, Na_2O and K_2O, are very similar. They are white deliquescent solids, which dissolve in water, forming strongly caustic alkaline solutions of the hydroxides. The chlorides, sulphates, nitrates, and carbonates have similar formulæ and very similar properties. Nearly all the salts of both metals are soluble in water.

CHAPTER XXXIII

CALCIUM AND ITS COMMON COMPOUNDS—HARDNESS OF WATER

Exp. 191—To make lime from limestone

Directions—Strongly heat some lumps of limestone in a muffle furnace. To the quicklime produced add a few drops of water, and notice the evolution of heat and the crumbling of the material.

Exp. 192—To examine bleaching powder

Directions—

(1) Shake up some bleaching powder with water and decant off the clear solution. Into it dip a piece of Turkey red cloth, and afterwards put the cloth into dilute hydrochloric acid for a few seconds. Wash the cloth, again dip it into the bleaching-powder solution, and then into the acid, and repeat the process until the cloth is bleached.

(2) Add dilute acid to bleaching powder, and test the evolved gas.

(3) To a solution of lead nitrate add sodium hydroxide solution until a thick precipitate of lead hydroxide is formed. To the mixture add bleaching-powder solution. Warm. What happens? Explain the action.

(4) Test for the presence of calcium chloride in bleaching powder by shaking a little of the powder with alcohol, filtering, and evaporating to dryness. Calcium chloride is soluble in alcohol.

Exp. 193—To make a standard soap solution, 1 c.c. of which shall be equivalent to one milligram of calcium carbonate

Directions—Dissolve about half a gram of pure calcium carbonate (Iceland spar) in dilute hydrochloric acid, and evaporate the solution to dryness on the water bath. Dissolve the residue of calcium chloride in as many c.c. of distilled water as you used milligrams of calcium carbonate, so that 1 c.c. of the calcium chloride solution is equivalent to one milligram of calcium carbonate.

Next dissolve about 2 grams of Castile soap in 200 c.c. of dilute alcohol (1 of alcohol to 2 of water). Mix the solution thoroughly.*

Place the soap solution in a burette. Put 20 c.c. of the calcium chloride solution into a stoppered bottle and add 50 c.c. of distilled water. Run in soap solution from the burette, and shake the bottle vigorously after each addition until you obtain a lather which is unchanged on standing for two minutes. Repeat the experiment. Next calculate the volume of the water to be added to dilute the soap solution until 21 c.c. of it would produce a permanent lather with 20 c.c. of the calcium chloride solution. Add the calculated volume of water to a known volume of soap solution. Then, 20 c.c. of the soap solution will precipitate 20 milligrams of calcium carbonate from solution in water. 1 c.c. of standard soap solution is required to produce a permanent lather with 70 c.c. of distilled water.

Exp. 194—To find the hardness of tap water

Directions—Find the hardness of the water in milligrams

* An alternative method is to dilute the soap solution until 14.25 c.c. of it will produce a permanent lather on 50 c.c. of a solution of calcium chloride, 1 c.c. of which corresponds to one-fifth of a milligram of calcium carbonate; 50 c.c. of the water are titrated, and the hardness in parts per 100,000 of water is found by reference to a hardness table.

of calcium carbonate per 70 c.c. by titration with standard soap solution. 1 c.c. must always be subtracted from the volume of the soap solution used, to allow for the excess of soap required to produce a permanent lather after precipitation of all the hardness.

The result gives the number of milligrams of calcium carbonate in 70 c.c. or 70,000 milligrams of water, *i.e.* parts by weight of hardness in 70,000 parts of water. A gallon of water weighs 70,000 grains. Therefore the number you have obtained will express the hardness in grains per gallon.

Exp. 195—To find the amounts of temporary and permanent hardness in hard water

Directions—Determine the total hardness. Then boil down 100 c.c. of the water to one-third of its bulk; make up the solution with distilled water to 100 c.c., and determine the permanent hardness of the solution. All the temporary hardness has been precipitated by the boiling. The amount of temporary hardness can be obtained by subtracting the permanent hardness from the total hardness.

Exp. 196—To test for the presence of calcium in calcium salts

Directions—

(1) Moisten the salt with strong hydrochloric acid, dip into it a platinum wire and heat the wire in the non-luminous bunsen flame. A red coloration indicates the presence of calcium.

(2) To a solution of a calcium salt add ammonium chloride, ammonium hydrate, and ammonium carbonate. A white precipitate of calcium carbonate is formed.

(3) To a solution of a calcium salt add calcium sulphate solution. No precipitate should be formed.

Exercises—

(1) Prepare specimens of calcium chloride, calcium sulphate, and calcium nitrate from chalk.

(2) Heat the powdered gypsum in an air oven to a temperature not exceeding 130° C. Mix the product to a paste with water, and allow the paste to stand.

CALCIUM, Ca=40

Calcium occurs in nature as carbonate, $CaCO_3$, in the forms *limestone*, *chalk*, *calcite*, etc.; as sulphate in *gypsum*, $CaSO_4.2H_2O$, and *anhydrite*, $CaSO_4$; as fluoride in *fluorspar*,

CaF_2; and as a double carbonate in *dolomite* or *magnesian limestone*, $CaCO_3.MgCO_3$.

Davy obtained the metal by electrolysis of the fused chloride. It is a soft white metal, which decomposes water at ordinary temperatures.

$$2H_2O + Ca = Ca(OH)_2 + H_2$$

Calcium oxide (*quicklime*), **CaO**—Lime is made by heating limestone in a lime kiln, Fig 122. The limestone is packed into the kiln in the manner shown in the figure, and heated strongly for some days by means of a fire under the arch. A good draught is necessary, in order to remove the carbon dioxide as fast as it is formed. Why must the carbon dioxide be removed? Various types of kiln are used.

$$CaCO_3 = CaO + CO_2$$

Properties—Pure lime is a white solid. It is infusible even in the oxyhydrogen blow-pipe flame. One part of lime dissolves in 700 parts of water. The solution is alkaline to litmus. When quicklime is treated with water, it gives out much heat and crumbles to a powder of slaked lime or calcium hydroxide, $Ca(OH)_2$. The slaked lime readily takes up carbon dioxide from the air, and forms calcium carbonate and water. Lime made into a cream with water is called *milk of lime*.

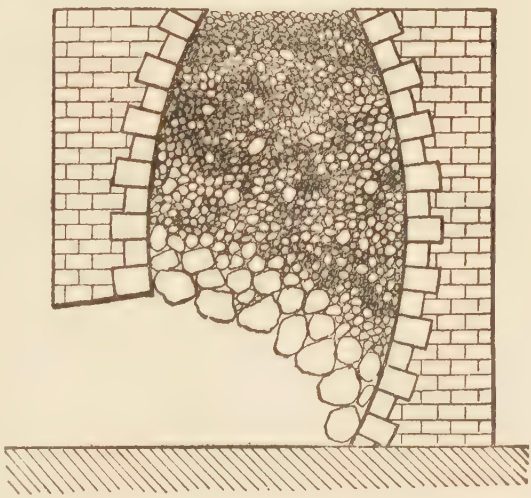


FIG. 122

Mortar consists of a mixture of slaked lime, sand, and water. The sand makes the mortar porous and less liable to crumble when it has set. Hardening of mortar is due to

the gradual formation of calcium carbonate through the action of the carbon dioxide of the air with the lime, and, to a much smaller extent, to the formation of calcium silicate by combination of lime and sand.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$
$$Ca(OH)_2 + SiO_2 = CaSiO_3 + H_2O$$

The water set free causes the plastered walls of new buildings to remain damp for many weeks.

Hydraulic cements are made by heating limestone containing some clay. They harden under water, possibly owing to the formation of a hydrated silicate of calcium and aluminium.

Calcium chloride, $CaCl_2$, is readily prepared by dissolving lime or limestone in hydrochloric acid.

$$CaO + 2HCl = CaCl_2 + H_2O$$

It is obtained as a waste product in the Solvay process for the manufacture of soda.

Properties—It is a deliquescent solid. The anhydrous salt is much used for drying gases. It is very soluble in water. The saturated solution deposits crystals of the formula $CaCl_2.6H_2O$.

Calcium chloride cannot be used for drying ammonia owing to the formation of the compound $CaCl_2.8NH_3$.

Bleaching powder, $CaOCl_2$—When chlorine is passed over slaked lime for some time, bleaching powder is obtained.

$$Ca(OH)_2 + Cl_2 = CaOCl_2 + H_2O$$

Properties—It is a yellowish white powder, almost entirely soluble in water. That it contains no free calcium chloride is shown by the fact that it is only slightly hygroscopic, and that calcium chloride is not dissolved out when bleaching powder is shaken with alcohol.

With dilute acids or carbon dioxide bleaching powder evolves chlorine—

$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2$$
$$CaOCl_2 + CO_2 = CaCO_3 + Cl_2$$

It is a good oxidising agent. Thus, when lead nitrate and manganese sulphate solutions are made alkaline with caustic soda, and treated with bleaching powder solution, lead peroxide and manganese dioxide respectively are formed.

$$(PbO)_2H_2O + 2CaOCl_2 = 2PbO_2 + 2CaCl_2 + H_2O$$
$$MnO.H_2O + CaOCl_2 = MnO_2 + CaCl_2 + H_2O$$

Bleaching powder is used for bleaching cotton goods, paper, etc. The material to be bleached is soaked in bleaching powder solution, and afterwards in dilute acid. The colouring matter is bleached by the chlorine set free in the fibre of the material.

Calcium sulphate, $CaSO_4$—This substance occurs in nature as gypsum, $CaSO_4.2H_2O$, and anhydrite, $CaSO_4$. It can be made in the laboratory by treating a strong solution of a calcium salt with dilute sulphuric acid.

$$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl$$

Properties—Calcium sulphate is a white solid, more suluble in cold than in hot water. Its solubility, even in cold water, is only very slight. When heated to 130° C., gypsum is converted to $(CaSO_4)_2.H_2O$, a white powder called *plaster of Paris*. Plaster of Paris, mixed with water, rapidly sets to a hard mass of $CaSO_4.2H_2O$ It is, therefore, valuable as a cement and for making casts.

$$(CaSO_4)_2.H_2O + 3H_2O = 2CaSO_4.2H_2O$$

Causes of hardness of water—The *temporary* hardness of water is due to the presence of calcium and magnesium bicarbonates in solution. These can be removed either by boiling the water or by addition of lime.

(1) Boiling. $\underset{\text{Calcium bicarbonate}}{Ca(HCO_3)_2} = \underset{\text{Insoluble}}{CaCO_3} + H_2O + CO_2$

(2) By addition of lime.

$$\underset{\text{Magnesium bicarbonate}}{Mg(HCO_3)_2} + CaO = \underbrace{CaCO_3 + MgCO_3}_{\text{Insoluble}} + H_2O$$

With soap the calcium and magnesium salts react, giving insoluble calcium and magnesium stearates, palmitates, and oleates, which float on the surface of the water as a curd.

$$Ca(HCO_3)_2 + 2\underset{\text{Sodium stearate}}{C_{17}H_{35}.COONa} = \underset{\text{Calcium stearate}}{(C_{17}H_{35}.COO)_2Ca} + 2NaHCO_3$$

*Permanent hardness** is due mainly to the presence in solution of sulphates and chlorides of calcium and magnesium. The reaction of calcium sulphate with soap gives insoluble calcium stearate, palmitate, and oleate.

$$CaSO_4 + 2C_{15}H_{31}.COONa = (C_{15}H_{31}.COO)_2Ca + Na_2SO_4$$

Sodium palmitate Calcium palmitate

Permanent hardness may be removed by addition of sodium carbonate, which precipitates insoluble calcium and magnesium carbonates.

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

The sodium sulphate does not react with the sodium salts of the soap.

The *permutite* process is a modern method of softening hard water. *Permutite* is a silicate of sodium and aluminium. Hard water is passed over permutite. The calcium and magnesium salts in the water react with the sodium silicate in the permutite forming calcium aluminium silicate and magnesium aluminium silicate. These silicates are reconverted to permutite by treatment with a strong solution of salt. The calcium and magnesium chlorides formed are washed away.

Tests for calcium—

(1) Calcium compounds moistened with strong hydrochloric acid, and held in a non-luminous flame on a platinum wire cause a red colour.

(2) A solution of a calcium salt, made alkaline with ammonium chloride and ammonium hydrate, gives a precipitate of calcium carbonate with ammonium carbonate solution.

$$CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl$$

(3) Solutions of calcium salts give no precipitate with calcium sulphate solution. This test serves to distinguish calcium from barium and strontium, which give precipitates with calcium sulphate.

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* The hard and compact " scale " or " fur " formed on boilers is due to the deposition of the temporary and permanent hardness of the water used, and may contain from 0 to 80 per cent. $CaCO_3$, and from 6 to 97 per cent. $CaSO_4$. In a boiler worked at a moderate pressure, a fairly typical scale would contain 56 per cent. $CaCO_3$; 32 per cent. $CaSO_4$; 7 per cent. $Mg(OH)_2$; 2.5 per cent. Fe_2O_3 and Al_2O_3; and 2.5 per cent. SiO_2 and other insoluble matter.

CHAPTER XXXIV

BARIUM AND ITS COMMON COMPOUNDS

Exp. 197—To test for barium

Directions—Carry out the following tests with a solution of a barium salt, and try to write equations for the reactions :—

(1) Add solutions of ammonium chloride, ammonia, and ammonium carbonate.

(2) Add solutions of ammonium chloride, ammonia, and ammonium oxalate.

(3) Add dilute sulphuric acid.

(4) Add calcium sulphate solution.

(5) Do the flame test.

Exercises—

(1) Prepare specimens of barium sulphate and carbonate from barium chloride.

(2) Prepare barium chloride and nitrate from the carbonate.

BARIUM, Ba = 137

Barium occurs in nature as the sulphate $BaSO_4$, in *heavy spar*, and as the carbonate in *witherite*, $BaCO_3$.

Matthiessen obtained the metal in small globules by electrolysis of the fused chloride. It is a white metal, which, like calcium, decomposes water at ordinary temperatures with formation of barium hydroxide and hydrogen.

Barium monoxide, **BaO** (*baryta*), can be prepared by heating the nitrate very strongly. It is obtained as a greyish white mass.

$$2Ba(NO_3)_2 = 2BaO + 4NO_2 + O_2$$

It may also be obtained by heating the carbonate or the iodate. It is strongly caustic and alkaline to litmus, and it combines with water with evolution of much heat and production of barium hydroxide. Heated to redness in air or oxygen, it takes up oxygen and forms barium dioxide, BaO_2.

It dissolves in acids, forming barium salts.

Barium dioxide, **BaO_2**, is obtained by heating the monoxide in air free from carbon dioxide and water vapour. It can be precipitated in the hydrated form by adding excess of baryta water to hydrogen peroxide.

$$Ba(OH)_2 + 6H_2O + H_2O_2 = BaO_2.8H_2O$$

The crystals of the hydrate can be converted to the anhydrous oxide by heating *in vacuo* to 130° C.

It is a greyish-white powder, which loses oxygen at bright red heat and forms the monoxide.

$$2BaO_2 = 2BaO + O_2$$

With dilute hydrochloric acid it forms hydrogen peroxide and barium chloride.

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2$$

Warmed in a stream of sulphur dioxide, it incandesces and forms barium sulphate.

$$BaO_2 + SO_2 = BaSO_4$$

It is used in the manufacture of oxygen by Brin's process.

Barium hydroxide, $Ba(OH)_2$, is obtained by treating the monoxide with water.

It is a white solid, which is more soluble in water than calcium hydroxide. The solution is called *baryta water*. Like lime water, baryta water reacts with carbon dioxide, forming a milky precipitate of barium carbonate.

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O$$

Barium chloride, $BaCl_2$, may be prepared by dissolving the carbonate in hydrochloric acid. It may also be obtained by heating barium sulphate strongly with carbon, and dissolving out the resulting sulphide with hydrochloric acid Thus—

$$BaSO_4 + 4C = BaS + 4CO$$
$$BaS + 2HCl = BaCl_2 + H_2S$$

It crystallises from solution in water in colourless rhombic tables, $BaCl_2.2H_2O$. It is fairly soluble in water, but it is almost insoluble in hydrochloric acid. It is very poisonous.

Barium carbonate, $BaCO_3$, occurs in nature as *witherite*. It is prepared in the laboratory by adding sodium or ammonium carbonate solution to a solution of a soluble barium salt.

$$BaCl_2 + Na_2CO_3 = BaCO_3 + 2NaCl$$

It is a white solid, which is very insoluble in water.

Barium sulphate, $BaSO_4$, occurs in nature as *barytes* or *heavy spar*, the latter name being given to it on account of its high specific gravity, 4.5. It separates as a white precipitate, when a soluble sulphate or dilute sulphuric acid is added to a solution of a barium salt.

$$BaCl_2 + K_2SO_4 = BaSO_4 + 2KCl$$

Barium sulphate is very insoluble in water and almost

insoluble in dilute acids. It dissolves in strong sulphuric acid, forming a solution from which an acid sulphate, $BaSO_4.H_2SO$, separates on cooling.

Precipitated barium sulphate is used as a white paint under the name of *permanent white.*

Barium nitrate, $Ba(NO_3)_2$, is prepared by dissolving the carbonate or sulphide in dilute nitric acid.

$$BaCO_3 + 2HNO_3 = Ba(NO_3)_2 + H_2O + CO_2$$

It crystallises from solution in large colourless octahedra. It is fairly soluble in water. When strongly heated, it splits into barium monoxide, nitrogen peroxide, and oxygen. It is used in firework manufacture for making *green fire.*

Tests for barium—

(1) Solutions of barium salts give a white precipitate of barium carbonate with ammonium carbonate solution in presence of ammonium chloride and ammonia.

(2) Solutions of barium salts give a white precipitate of barium oxalate with ammonium oxalate solution in presence of ammonium chloride and ammonia.

$$BaCl_2 + (NH_4)_2C_2O_4 = BaC_2O_4 + 2NH_4Cl.$$

(3) Dilute sulphuric acid precipitates white barium sulphate from solutions of barium salts.

(4) Calcium sulphate solution produces immediately a white precipitate of barium sulphate in solutions of barium salts.

(5) Barium salts colour the bunsen flame light green.

Similarity of calcium and barium

It will have been noticed that both metals are soft and white, and that they decompose water at ordinary temperatures. They are also easily oxidised by the oxygen of the air.

Their compounds are also very much alike. Both form two oxides, the monoxide in each case being very stable, slightly soluble in water, and alkaline to litmus. Their sulphates are both insoluble, their carbonates are insoluble, and their chlorides and nitrates are soluble. Both metals act as diads in their salts. This great similarity is in accordance with their position in the same sub-group in Group II of the Periodic Classification.

CHAPTER XXXV

COPPER AND ITS COMMON COMPOUNDS

Exp. 198—To observe the reactions of copper salts with various reagents

Directions—Carry out the following tests with a solution of a copper salt, and try to write the equations for the reactions taking place :—

(1) Acidify a solution of a copper salt with hydrochloric acid, and pass sulphuretted hydrogen through the solution.

(2) Add excess of caustic soda to a cold solution of a copper salt. Afterwards boil.

(3) Add excess of ammonium hydroxide solution.

(4) Add a strip of sheet iron or zinc, and allow to stand.

(5) Add potassium ferrocyanide solution.

(6) Do the flame test for copper.

(7) Mix a little powdered copper salt with potassium cyanide, and heat the mixture on charcoal with the blow-pipe.

Exp. 199—To prepare cuprous oxide and cuprous chloride

Directions—Make some Fehling's solution by dissolving about 5 grams of copper sulphate in water, and adding a solution of a mixture of 25 grams of Rochelle salt with 10 grams of caustic soda.

To the Fehling's solution add a small quantity of a solution of glucose and warm gently. Filter off and wash the cuprous oxide precipitated.

Warm half of the oxide with *dilute* sulphuric acid, and note the character of the solution and of the residue.

Dissolve the rest of the oxide in a few c.c. of strong hydrochloric acid, and pour the solution into water. The white precipitate is cuprous chloride. Dissolve it in ammonia and blow air through the solution. What happens ?

Exercises—Prepare cupric oxide from a copper salt, and prepare specimens, crystalline if possible, of cupric chloride, sulphate, and nitrate from cupric oxide.

COPPER, Cu. Atomic weight=63

Occurrence—Copper occurs in the metallic condition in large quantities near Lake Superior, and in smaller quantities

in various parts of the world. Its chief ores are *ruby copper* or *cuprite* Cu_2O, *copper glance* Cu_2S, *copper pyrites* $Cu_2S.Fe_2S_3$, *malachite* $CuCO_3.Cu(OH)_2$, and *azurite* $2CuCO_3.Cu(OH)_2$.

Extraction—Copper is extracted from its ores by the process of self-reduction. The ores are alternately oxidised by roasting in reverberatory furnaces, and fused with materials which are capable of combining with the iron oxide formed by oxidation of the sulphide of iron in the ore.

The main reaction during roasting is—

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$

When fused, the cuprous oxide reacts with the cuprous sulphide.

$$Cu_2S + 2Cu_2O = 6Cu + SO_2$$

The impurity of iron oxide goes into the slag and is removed.

The impure copper is melted down in an oxidising atmosphere to remove impurities of arsenic, iron, and lead, and the molten metal is finally stirred with poles of green wood to reduce oxides of copper to metal.

Properties—Copper is a bright metal of a reddish-brown colour. It is very tough, and it can be drawn into wire or hammered into thin leaf. Its specific gravity is nearly 9. It is an excellent conductor of heat and electricity. At temperatures near its melting-point it becomes sufficiently brittle to be powdered. It melts at 1050° C.

Copper is not attacked by dry air, but when exposed to the atmosphere it gradually becomes coated with a green basic carbonate, *verdigris*. Heated in air, it becomes coated with a black scale of cupric oxide.

Hydrochloric acid and cold sulphuric acid have very little action on copper, but hot, strong sulphuric acid reacts with it, forming copper sulphate, sulphur dioxide, and a dark residue of sulphides of copper. The chief reaction is—

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$

With dilute or strong nitric acid copper readily reacts, forming copper nitrate and oxides of nitrogen. The reaction with cold dilute nitric acid is—

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$

Copper is largely used for electric cables and wires.

Copper forms two oxides, cuprous oxide Cu_2O, and cupric oxide CuO. Corresponding to these oxides there are cuprous salts and cupric salts.

Cuprous oxide, Cu_2O, occurs native as ruby ore. It is readily prepared by reduction of Fehling's solution with glucose. Fehling's solution may be regarded as a solution of cupric oxide.

$$2CuO - O = Cu_2O$$

Properties—Cuprous oxide is a red powder. It dissolves in strong hydrochloric acid, and forms a colourless solution of cuprous chloride.

$$Cu_2O + 2HCl = Cu_2Cl_2 + H_2O$$

With dilute sulphuric acid it reacts as if it were a mixture of metallic copper and cupric oxide. Copper sulphate is formed and copper is set free.

$$Cu_2O + H_2SO_4 = CuSO_4 + H_2O + Cu$$

Cuprous oxide dissolves in molten glass and imparts to it a fine ruby colour.

Cupric oxide, CuO, is prepared by heating the hydroxide, carbonate, or nitrate of the metal.

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

Properties—Cupric oxide is a black powder much used in organic chemistry for the oxidation of the carbon and hydrogen of organic compounds to carbon dioxide and water respectively.

When it is heated in a stream of carbon monoxide or hydrogen it is reduced to metal.

$$CuO + CO = Cu + CO_2$$

It dissolves in acids, forming cupric salts.

Copper hydroxide, $Cu(OH)_2$, is obtained as a pale blue precipitate when excess of caustic soda is added to a *cold* solution of a cupric salt.

$$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4$$

When the mixture is boiled, the hydroxide is converted into a black hydrate, $Cu(OH)_2.2CuO$. Copper hydroxide dissolves in ammonia, forming a deep blue solution, which is a solvent for cellulose.

Cuprous chloride, Cu_2Cl_2, is obtained by dissolving cuprous

oxide in strong hydrochloric acid, or by boiling a solution of cupric chloride with copper and hydrochloric acid. In each case the cuprous chloride is precipitated by pouring the solution into excess of water.

$$Cu_2O + 2HCl = Cu_2Cl_2 + H_2O \qquad CuCl_2 + Cu = Cu_2Cl_2$$

Properties—Cuprous chloride is a white solid, insoluble in water, but easily soluble in hydrochloric acid or ammonia. These solutions on exposure to air absorb oxygen, and deposit a greenish basic chloride or oxychloride of copper, $CuCl_2.3CuO.4H_2O$. The solution in ammonia is a solvent for carbon monoxide, and is used for separating that gas from other gases. The ammonia solution also reacts with acetylene, forming a red precipitate of copper acetylide, $Cu_2O.C_2H_2$.

The vapour density of cuprous chloride corresponds to the formula Cu_2Cl_2.

Cupric chloride, $CuCl_2$, is prepared by dissolving cupric oxide, carbonate, or hydroxide in hydrochloric acid.

$$Cu(OH)_2 + 2HCl = CuCl_2 + 2H_2O$$

Properties—Cupric chloride crystallises from solution in water in green prisms, $CuCl_2.2H_2O$. The solution is green when strong, but blue when dilute. When crystalline cupric chloride is heated it loses its water, and at a red heat splits into cuprous chloride and chlorine.

$$2CuCl_2 = Cu_2Cl_2 + Cl_2$$

The dark blue solution of the salt in ammonia deposits, on evaporation, blue crystals of the composition $CuCl_2.4NH_3.H_2O$.

Cupric sulphate, $CuSO_4$, is prepared by dissolving cupric oxide in dilute sulphuric acid.

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

Properties—Copper sulphate crystallises from solution in water in blue crystals, $CuSO_4.5H_2O$. These are known in commerce as *blue vitriol*. When crystalline copper sulphate is heated it is converted at 100° C. into a bluish-white salt, $CuSO_4.H_2O$, and at 240° C. into the white anhydrous salt, $CuSO_4$. The white salt is useful for the detection of small quantities of water, and for the removal of traces of water from organic liquids. With water it again forms the blue salt.

When heated more strongly, copper sulphate forms a yellow basic sulphate, $CuSO_4.CuO$.

The deep blue solution, obtained by adding ammonia to copper sulphate solution, deposits, on evaporation, blue crystals of $CuSO_4.4NH_3.H_2O$. Copper sulphate solution is used in the Daniell cell and for electrolytic copper plating.

Cupric nitrate, $Cu(NO_3)_2$, is obtained by dissolving copper or copper oxide in nitric acid.

$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O$$

Properties—It crystallises from solution in deep blue crystals $Cu(NO_3)_2.3H_2O$. It is deliquescent. The salt cannot be obtained in the anhydrous state, because the crystals at 65° C. lose nitric acid and water and give the basic nitrate.

$$4Cu(NO_3)_2.3H_2O = Cu(NO_3)_2.3Cu(OH)_2 + 6HNO_3 + 6H_2O$$

When heated more strongly, copper nitrate breaks up entirely.

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

Tests for copper—

(1) Sulphuretted hydrogen gives, with solutions of copper salts, a black precipitate of copper sulphide, CuS.

(2) Excess of caustic soda solution gives, with copper salts in the cold, a blue precipitate of copper hydroxide, $Cu(OH)_2$; and on boiling, a black precipitate of $Cu(OH)_2.2CuO$.

(3) Ammonium hydroxide produces a deep blue solution.

(4) Zinc and iron precipitate metallic copper from solutions of its salts.

$$Zn + CuSO_4 = Cu + ZnSO_4$$
$$Fe + CuCl_2 = Cu + FeCl_2$$

(5) Potassium ferrocyanide gives a chocolate-coloured precipitate of copper ferrocyanide, $Cu_2Fe(CN)_6$.

(6) Copper salts, moistened with strong hydrochloric acid, colour the non-luminous flame green, with a flash of blue when the platinum wire is first put into the flame.

(7) Copper compounds, heated on charcoal with potassium cyanide, are reduced to metallic copper.

$$CuO + KCN = Cu + KCNO$$

CHAPTER XXXVI

MERCURY AND ITS COMMON COMPOUNDS

Exp. 200—To test for mercurous compounds

Directions—Carry out the following tests with a solution of a mercurous salt, and try to write the equations for the reactions :—

(1) Add dilute hydrochloric acid, and then ammonia solution.

(2) Add caustic soda solution.

(3) Add excess of stannous chloride solution.

(4) Add potassium iodide solution.

(5) Heat a solid mercurous compound with powdered charcoal and sodium carbonate in a small tube.

Exp. 201—To test for mercuric compounds

Directions—Carry out the following tests with a solution of a mercuric salt, and try to write the equations for the reactions :—

(1) Acidify with dilute hydrochloric acid, and then pass a slow current of sulphuretted hydrogen through the solution.

(2) Add caustic soda solution.

(3) Add excess of stannous chloride solution.

(4) Add potassium iodide solution.

(5) Heat a solid mercuric compound with powdered charcoal and sodium carbonate in a small tube.

Exp. 202—To prepare mercuric oxide and from it prepare mercury

Directions—Heat gently a few grams of mercuric nitrate in an evaporating dish in a draught chamber until no more red fumes of nitrogen peroxide come off. Find out in what acids the resulting mercuric oxide is soluble.

Heat strongly the remaining mercuric oxide in a hard glass tube placed in a horizontal position. Collect the mercury, and find out its reactions with acids.

Exercises—

(1) Prepare specimens of mercuric chloride and nitrate from mercuric oxide.

(2) Try to prepare a specimen of mercurous chloride by addition of stannous chloride to excess of mercuric chloride solution.

MERCURY, Hg=200

Occurrence—Mercury is found in the free state in small quantities in nature. It occurs chiefly as *cinnabar*, HgS.

Extraction—Mercury is extracted from cinnabar by roasting the ore in air in a suitable furnace.

$$2HgS + 2O_2 = 2Hg + 2SO_2$$

The mercury is condensed in flues and chambers. It is then collected and freed from dust and grit by straining through chamois leather. Dissolved impurities can be removed by distillation.

Properties—Mercury is a silver-white liquid metal; hence the name *quicksilver*. It solidifies at $-39°$ C. to a crystalline solid, which is malleable and ductile and softer than lead. At 0° C. the specific gravity of mercury is 13.59. Its vapour density is 100. Its molecular weight is, therefore, 200, the same as its atomic weight. Therefore, the molecule of mercury contains only one atom. Mercury boils at 357° C. Its vapour is poisonous.

Mercury is unacted upon by air and by many other gases. It is, therefore, most useful for collecting gases, which are soluble in water. When heated in air to a temperature near its boiling-point for a long time, it is oxidised to mercuric oxide.

The metal is unattacked by hydrochloric acid, but dilute nitric acid dissolves it slowly in the cold with formation of mercurous nitrate. Strong nitric acid dissolves it rapidly, forming mercuric nitrate and oxides of nitrogen. It is unattacked by cold, strong, sulphuric acid, but with hot, strong, sulphuric acid it forms mercuric sulphate and sulphur dioxide.

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2$$

Mercury is used for making thermometers on account of its convenient boiling and freezing-points and its uniform expansion under increase of temperature. It is also used largely for making amalgams.

Mercurous oxide, Hg_2O, is a dark powder obtained by warming mercurous chloride with caustic soda.

$$Hg_2Cl_2 + 2NaOH = 2NaCl + H_2O + Hg_2O$$

If mercurous oxide is heated or exposed to light, it splits into mercuric oxide and mercury.

$$Hg_2O = HgO + Hg$$

Mercuric oxide, **HgO**, may be prepared by heating mercuric nitrate carefully.

$$2Hg(NO_3)_2 = 2HgO + 4NO_2 + O_2$$

It is prepared on the large scale by heating a mixture of mercuric nitrate and mercury.

Mercuric oxide is a red crystalline powder when prepared by the above methods, but it is precipitated as an orange amorphous powder when caustic soda solution is added to a solution of a mercuric salt. If heated gently, it darkens until it is almost black, but it regains its original colour on cooling. If heated strongly, it breaks up into mercury and oxygen.

It dissolves in acids forming mercuric salts.

Mercurous chloride (*calomel*), Hg_2Cl_2, falls as a white precipitate when hydrochloric acid, or a solution of a soluble chloride, is added to mercurous nitrate solution.

$$Hg_2(NO_3)_2 + 2HCl = Hg_2Cl_2 + 2HNO_3$$

On the large scale it is prepared by heating a mixture of mercuric chloride and mercury. The calomel sublimes as a white fibrous cake.

Properties—Mercurous chloride is a white tasteless solid, which is insoluble in water. It has been proved that mercurous chloride, when vaporised, splits up into mercuric chloride and mercury Consequently, its vapour density corresponds to the formula HgCl. Baker has, however, shown that perfectly dry calomel has a normal vapour density, corresponding to the formula Hg_2Cl_2.

When exposed to strong daylight, or boiled with hydrochloric acid, mercurous chloride is transformed into mercuric chloride and mercury.

With ammonia solution mercurous chloride gives a black powder, NH_2Hg_2Cl, which may be regarded as ammonium

chloride, in which two hydrogen atoms have been replaced by two mercury atoms.

$$Hg_2Cl_2 + 2NH_3 = NH_2Hg_2Cl + NH_4Cl$$

Mercuric chloride (*corrosive sublimate*), $HgCl_2$, can be prepared by passing chlorine over heated mercury, by dissolving mercury in *aqua regia*, and by dissolving mercuric oxide in hot hydrochloric acid.

$$HgO + 2HCl = HgCl_2 + H_2O$$

On the large scale it is made by subliming a mixture of common salt and mercuric sulphate.

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4$$

Properties—Mercuric chloride is somewhat soluble in water to an acid solution, from which it crystallises in long silky needles. It melts and volatilises unchanged. It is a strong poison, and it is a good antiseptic. With ammonia, mercuric chloride gives a white precipitate (infusible white precipitate), NH_2HgCl, which may be regarded as ammonium chloride, in which two atoms of hydrogen have been replaced by one mercury atom.

$$HgCl_2 + 2NH_3 = NH_2HgCl + NH_4Cl$$

Mercurous sulphate, Hg_2SO_4, falls as a white crystalline precipitate when dilute sulphuric acid is added to a solution of mercurous nitrate. It is slightly soluble in water.

Mercuric sulphate, $HgSO_4$, can be made by heating mercury with strong sulphuric acid in a draught chamber.

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2$$

It is a white solid, which is decomposed by boiling water into an acid sulphate and an insoluble basic salt, $HgSO_4.2HgO$. The latter is known as *turpeth mineral*.

Mercurous nitrate, $Hg_2(NO_3)_2$, is obtained as the hydrated salt, $Hg_2(NO_3)_2.2H_2O$, when a solution of mercury in cold dilute nitric acid is evaporated at ordinary temperatures. The salt is soluble in water acidified with dilute nitric acid, but it is decomposed by ordinary water with formation of a basic salt, $Hg_2(NO_3)_2.Hg_2O.H_2O$.

Mercuric nitrate, $Hg(NO_3)_2$, is made by boiling nitric acid with mercury until a test portion gives no precipitate with

hydrochloric acid. If this solution is evaporated *in vacuo* over sulphuric acid, crystals of the composition $2Hg(NO_3)_2.H_2O$ are obtained. These crystals are deliquescent, and with water form insoluble basic nitrates.

Mercuric iodide, HgI_2, is obtained as a yellow precipitate, which almost immediately changes to scarlet when a mercuric salt is treated with a solution of potassium iodide.

$$HgCl_2 + 2KI = HgI_2 + 2KCl$$

Mercuric iodide is insoluble in water, but it dissolves in potassium iodide solution, or in alcohol, or in nitric acid. From these solutions it is deposited in scarlet crystals. If the dry scarlet crystals are heated somewhat above 150° C., they are changed to bright yellow crystals. The yellow form is unstable at ordinary temperatures. When it is touched, it changes back into the scarlet form. The yellow form is, however, the more stable form at the temperature of evaporating liquid oxygen. A substance, which exists in two distinct crystalline forms, is said to be *dimorphous*.

Mercuric sulphide, HgS, also exists in two forms, but only one is crystalline. It is obtained as a black amorphous precipitate when sulphuretted hydrogen is passed through a solution of a mercuric salt. The amorphous form can be changed into a red crystalline form by sublimation, or by digesting with ammonium sulphide solution for some hours. The red variety is made on the large scale for use as the pigment *vermilion*.

Tests for mercury—(1) With hydrochloric acid, mercurous salts form a white precipitate of mercurous chloride, which blackens with ammonia. Mercuric salts give no precipitate.

(2) With caustic soda, mercurous salts form a black precipitate of mercurous oxide, and mercuric salts form an orange precipitate of mercuric oxide.

(3) Stannous chloride solution forms with mercurous salts a greyish-black precipitate of mercury: with mercuric salts a white precipitate of mercurous chloride is first produced, which, with stannous chloride in excess, gradually changes to a grey precipitate of mercury.

(4) Potassium iodide produces a greenish precipitate of mercurous iodide with mercurous salts, and a scarlet precipitate of mercuric iodide with mercuric salts.

(5) Both mercurous and mercuric salts, when heated with powdered charcoal and sodium carbonate in a small tube, give a mirror of metallic mercury on the cold part of the tube.

(6) If sulphuretted hydrogen is passed through an acidified solution of a mercuric salt, a precipitate is produced which changes from white to orange, from orange to brownish-red, and then to black. The precipitate is mercuric sulphide, HgS

CHAPTER XXXVII

MAGNESIUM AND ITS COMMON COMPOUNDS

Exp. 203—To test for magnesium

Directions—

(1) To a solution of a magnesium salt add solutions of ammonium chloride, ammonia, and sodium phosphate.

(2) Heat a solid magnesium compound on charcoal before the blow-pipe. Moisten the resulting mass with a solution of cobalt nitrate, and heat again.

Exp. 204—To prepare anhydrous magnesium chloride from the oxide

Directions—Dissolve a few grams of the oxide in dilute hydrochloric acid. A solution of magnesium chloride, on evaporation, yields a mixture of magnesium chloride and oxide, owing to the partial decomposition of the magnesium chloride by the water. To prevent this, add to your solution excess of ammonium chloride solution. The mixture, on evaporation to dryness, yields a double salt of the formula $MgCl_2.NH_4Cl$. From this the ammonium chloride can be driven off by heating in a draught chamber, when magnesium chloride, free from oxide, is left.

Exercises—

(1) Make magnesium oxide from the metal.

(2) Prepare a crystalline specimen of magnesium sulphate from the oxide.

MAGNESIUM, Mg=24

Magnesium occurs in nature as *magnesite*, $MgCO_3$, as *dolomite*, $MgCO_3.CaCO_3$, as *carnallite*, $KCl.MgCl_2.6H_2O$, as

kieserite, $MgSO_4.H_2O$, and as silicates in *asbestos*, *hornblende*, *talc*, *steatite*, and *serpentine*.

The metal can be obtained by electrolysis of the fused chloride, or by heating the chloride with sodium. The metal can be purified by distillation.

Properties—Magnesium is a silver-white metal, which is not affected by dry air, but is tarnished by moist air. Its specific gravity is only 1.74. It melts at a red heat. It burns in air with a dazzling white light, which is rich in chemically active rays. Hence it is used as a flash light for photographic purposes. It is fairly malleable, and it is ductile near its melting-point. It is readily soluble in acids, with which it reacts like zinc (*q.v.*). Magnesium differs from zinc in its action with dilute nitric acid, from which in the cold it sets free hydrogen.

$$Mg + 2HNO_3 = Mg(NO_3)_2 + H_2$$

It differs from zinc also in being unattacked by caustic alkalis. Like zinc it is strongly electropositive, and will displace less electropositive metals from solutions of their salts.

$$Mg + 2AgNO_3 = Mg(NO_3)_2 + 2Ag$$

Magnesium oxide, **MgO** (*magnesia*), is formed when the metal burns in air, or when magnesium carbonate is heated strongly. Obtained by the second method, it is a bulky white powder, which is known commercially as *calcinea magnesia* or *magnesia usta*.

Properties—Magnesia is almost insoluble in water, but sufficiently soluble for its solution to turn red litmus blue. Its infusibility renders it valuable for making crucibles and cupels. It dissolves readily in acids, neutralising them and forming salts.

Magnesium hydroxide $Mg(OH)_2$, is prepared by precipitating a solution of a magnesium salt with caustic soda.

$$MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4$$

It is a white solid, which gives up its water at a dull red heat, forming the oxide. It absorbs carbon dioxide slowly from the air, forming the carbonate.

Magnesium chloride, $MgCl_2$, can be obtained in the hydrated

form by dissolving the oxide or carbonate in hydrochloric acid and evaporating the solution to the crystallising point. Deliquescent crystals, $MgCl_2.6H_2O$, are obtained. The anhydrous chloride is obtained in the manner described in Exp. 204.

If a solution of the chloride is evaporated to dryness, some hydrochloric acid is given off, and the residue is found to contain some magnesia. If a strong solution of the chloride is mixed with magnesium oxide and a small quantity of water, the mass sets quickly to a hard mass which contains a basic chloride, $MgCl_2.5MgO$.

Magnesium sulphate, $MgSO_4.7H_2O$ (*Epsom salts*), is prepared by dissolving the metal, oxide, hydroxide, or carbonate in dilute sulphuric acid and evaporating the solution to the crystallising point.

$$MgO + H_2SO_4 = MgSO_4 + H_2O$$

Properties—Magnesium sulphate crystallises from solution as colourless prisms, $MgSO_4.7H_2O$, isomorphous with $ZnSO_4.7H_2O$, and known as *Epsom salts*. These crystals lose six molecules of water at 150° C., and the seventh molecule at 200° C. Magnesium sulphate is very soluble in water, its solubility at ordinary temperatures being about 120. The solution has a bitter taste. It acts as a purgative. Magnesium sulphate forms double sulphates with alkaline sulphates, *e.g.* $MgSO_4.K_2SO_4.6H_2O$.

Magnesium carbonate, $MgCO_3$, occurs native as *magnesite*. It cannot be obtained by adding a solution of a soluble carbonate to a solution of a magnesium salt, the white precipitate obtained in this way being a basic carbonate.

Magnesium ammonium phosphate, $MgNH_4PO_4\,6H_2O$, is obtained as a crystalline precipitate, when sodium phosphate solution is added to a solution of magnesium sulphate made alkaline by the addition of ammonium chloride and ammonia. If the salt is heated strongly, it gives off water and ammonia and leaves a residue of magnesium pyrophosphate.

$$2MgNH_4PO_4.6H_2O = Mg_2P_2O_7 + 2NH_3 + 13H_2O$$

Tests for magnesium—

(1) The formation of magnesium ammonium phosphate in the above manner serves as a test for magnesium.

(2) Magnesium compounds heated on charcoal, afterwards moistened with cobalt nitrate solution, and then re-heated, produce a pale pink infusible mass.

Similarity of zinc and magnesium—These two metals are in the same sub-group of the Periodic Classification. We should, therefore, expect them and their compounds to have similar properties. This is the case. Both are white, rather brittle metals, which burn brilliantly in air, forming white infusible oxides. They react in similar ways with acids, forming products which are also similar.

Their oxides and hydroxides are insoluble in water, but easily soluble in acids ; their chlorides are soluble and partially decomposed to the oxides when their solutions are evaporated to dryness ; their carbonates are insoluble, and their sulphates are isomorphous with one another. The properties of the elements and their compounds correspond, in fact, to what would be expected from the relative positions of the metals in the Periodic Classification.

CHAPTER XXXVIII

ZINC AND ITS COMMON COMPOUNDS

Exp. 205—To observe some of the reactions of zinc salts

Directions—Carry out the tests 1 and 2 with a solution of a zinc salt, and try to write equations for the reactions.

(1) Make the solution alkaline by adding ammonium chloride and ammonium hydroxide solutions, and then add ammonium sulphide solution.

(2) Add a few drops of caustic soda solution, and afterwards excess of the reagent.

(3) Heat a solid zinc salt with sodium carbonate on charcoal before the blow-pipe and note the colour change that takes place on cooling. Afterwards add to the resulting mass one or two drops of cobalt nitrate solution and heat once more.

Exercises—Make zinc oxide from zinc, in any way you can think of, and prepare from zinc oxide specimens of zinc sulphate, chloride, and sulphide.

ZINC, Zn. Atomic weight=65

Occurrence—The chief ores of zinc are *zinc blende*, ZnS, and *calamine*, $ZnCO_3$.

Extraction—Zinc is obtained by roasting the ores in a current of air to convert them to oxide, and reducing the oxide by heating with carbon.

$$ZnCO_3 = ZnO + CO_2$$
$$2ZnS + 3O_2 = 2ZnO + 2SO_2$$
$$ZnO + C = Zn + CO$$

The zinc oxide is heated to bright redness with carbon in earthenware retorts. The zinc distils over and collects in iron receivers.

Commercial zinc usually contains impurities of iron, carbon, lead, cadmium, and sometimes arsenic and copper.

Properties—Zinc is a bluish-white, crystalline, brittle metal, which tarnishes in damp air. At 120–150° C. it is malleable and may be rolled into sheets. It melts at 420° and boils below 1000° C. Its specific gravity is about 7. Its vapour density is 32.5, corresponding to a molecular weight of 65; therefore its molecule is monatomic. It burns in air with a dazzling, bluish-white flame, forming the oxide ZnO as a white flocculent substance, which was formerly known as *philosopher's wool*.

Zinc dissolves readily in dilute hydrochloric and sulphuric acids, forming salts and hydrogen. With hot, strong sulphuric acid it causes evolution of sulphur dioxide.

$$Zn + 2H_2SO_4 = ZnSO_4 + 2H_2O + SO_2$$

With dilute nitric acid it gives fairly pure nitrous oxide.

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + N_2O + 5H_2O$$

With strong nitric acid the reaction is—

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

Zinc also dissolves in strong caustic potash solution.

$$Zn + 2KOH = K_2ZnO_2 + H_2$$

Potassium zincate

Zinc is a strongly electropositive metal. It precipitates the

less electropositive metals, silver, copper, lead, etc., from solutions of their salts.

$$Pb(NO_3)_2 + Zn = Pb + Zn(NO_3)_2$$

A zinc-copper couple, *i.e.* zinc coated with copper by immersion in a solution of copper sulphate, readily decomposes hot water.

$$Zn + H_2O = ZnO + H_2$$

The copper is unchanged.

Zinc is used largely for *galvanising* iron. Sheets of clean iron are dipped into a bath of molten zinc. The coating of zinc, as long as it is intact, prevents the rusting of the iron.

Zinc oxide, **ZnO**, is prepared by precipitating and heating the hydroxide or carbonate. On the large scale it is prepared by burning zinc and collecting the fumes in condensing chambers.

Properties—Zinc oxide is a white solid, which becomes yellow on heating and white once more on cooling. It is insoluble in water, and does not combine with water to give the hydroxide. It readily dissolves in acids, forming salts.

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O$$

It is manufactured under the name of *zinc white*. White paint made with zinc white does not blacken like white lead on exposure to sulphuretted hydrogen. Zinc white does not, however, equal white lead in *body*, *i.e.* covering power.

Zinc hydroxide, $Zn(OH)_2$, is prepared by precipitating a solution of a zinc salt with caustic soda.

$$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4$$

Excess of caustic soda must not be used; otherwise the hydroxide will be redissolved, owing to the formation of sodium zincate, $Zn(ONa)_2$. When the hydroxide is heated, it gives the oxide.

$$Zn(OH)_2 = ZnO + H_2O$$

Zinc chloride, $ZnCl_2$, can be obtained by dissolving the metal, oxide, hydroxide, or carbonate in hydrochloric acid.

$$ZnO + 2HCl = ZnCl_2 + H_2O$$

Properties—Zinc chloride crystallises from aqueous solution in deliquescent crystals, $ZnCl_2.H_2O$. When an aqueous solution of zinc chloride is evaporated, partial decomposition

takes place, hydrochloric acid is evolved, and basic chlorides are produced. Hence, in the manufacture of zinc chloride, hydrochloric acid is added from time to time to replace the acid driven off during evaporation. The anhydrous chloride is a soft, easily fusible solid, which is very deliquescent and is a powerful dehydrating agent.

If zinc oxide is mixed to a paste with strong zinc chloride solution, the mixture sets to a white mass, which is so hard that it can be used as a stopping for teeth.

Zinc sulphate, $ZnSO_4.7H_2O$ (*white vitriol*), is prepared by dissolving the metal, oxide, hydroxide, or carbonate in dilute sulphuric acid and evaporating the solution to the crystallising point.

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O$$

Properties—Zinc sulphate crystallises from solution in colourless prisms, $ZnSO_4.7H_2O$. These crystals lose six molecules of water at 100° C., and the seventh molecule at 300° C. Zinc sulphate is extremely soluble in water, and the solution has an astringent taste. At 100° C., 100 parts of water dissolve 650 parts of the crystallised salt. Zinc sulphate forms double sulphates with potassium and ammonium sulphates, *e.g.* $ZnSO_4.K_2SO_4.6H_2O$.

Zinc sulphide, ZnS, occurs in nature as *zinc blende*. It can be obtained as a white precipitate by adding ammonium sulphide solution to a solution of a zinc salt.

$$ZnSO_4 + (NH_4)_2S = ZnS + (NH_4)_2SO_4$$

It is a white solid, insoluble in water, but soluble in dilute acids.

$$ZnS + 2HCl = ZnCl_2 + H_2S$$

Tests for zinc—

(1) Ammonium sulphide, when added to an alkaline solution of a zinc salt, gives a white precipitate of zinc sulphide, ZnS.

(2) Sodium hydroxide gives, with a solution of a zinc salt, a precipitate of the hydroxide $Zn(OH)_2$, which is soluble in excess of the reagent with formation of sodium zincate, Na_2ZnO_2 or $Zn(ONa)_2$.

(3) Zinc compounds, heated on charcoal alone, or with sodium carbonate, give a yellow crust of zinc oxide which becomes white on cooling. If cobalt nitrate solution is added,

and the zinc oxide reheated, a green mass called *Rinmann's green* is obtained.

CHAPTER XXXIX

IRON AND ITS COMMON COMPOUNDS

Exp. 206—To observe some of the reactions of ferrous and ferric salts

Directions—Carry out the following tests with solutions of ferrous and ferric salts—

(1) Add ammonium chloride and ammonium hydroxide solutions.

(2) Add potassium ferrocyanide solution.

(3) Add a freshly made solution of potassium ferricaynide.

(4) Add potassium sulphocyanate solution.

(5) Heat borax on a loop made in a platinum wire until a clear, colourless bead is formed. Dip this bead, when hot, into a very small quantity of the solid salt, and heat it in the reducing flame of the bunsen burner. Heat the bead you obtain in the oxidising flame, and note any colour change.

Exp. 207—To prepare the oxides of iron

Directions—

(1) Make ferrous oxide by heating ferrous oxalate in a hard glass tube. After noting the appearance of the oxide, shake out a little into the air. What happens? Dissolve the remaining oxide in hydrochloric acid, and test the solution for a ferrous salt.

(2) Make ferric oxide from ferrous sulphate solution. Acidify the solution with sulphuric acid, add a few c.c. of strong nitric acid, and heat with constant stirring until the solution becomes a clear yellow. The iron has now been oxidised to ferric sulphate. Precipitate ferric hydroxide by adding excess of ammonium hydroxide. Wash and heat the ferric hydroxide. Note the appearance of the oxide. Dissolve some of it in hydrochloric acid and test for a ferric salt.

(3) Make hydrated magnetic iron oxide from ferrous sulphate solution. Oxidise two-thirds of the solution to ferric sulphate, cool down thoroughly, and add the remaining third. The cooling is necessary to prevent oxidation of the ferrous

sulphate in the remaining third by the nitric acid. Next add ammonium hydroxide until the liquid smells of ammonia. Boil. Wash the precipitated magnetic oxide by decantation and test it with a magnet.

EXERCISES

Prepare ferrous sulphate from iron, taking precautions to prevent oxidation by the air; prepare ferric sulphate and ferric chloride from ferric oxide; prepare ferrous sulphide by direct combination of iron and sulphur; and attempt to prepare anhydrous ferric chloride by heating iron wire very strongly in a hard glass tube, through which passes a current of chlorine.

IRON, Fe. Atomic weight = 56

Occurrence—Iron is one of the most widely distributed elements. In the metallic form it is found in large masses in Greenland, and in small particles disseminated through some basalts. It is also found associated with cobalt and nickel in meteorites. Its chief ores are *red hæmatite* Fe_2O_3, *specular iron ore* Fe_2O_3, *brown hæmatite* or *limonite* $2Fe_2O_3.3H_2O$, *magnetite* Fe_3O_4, *spathic iron ore* $FeCO_3$, and *clay ironstone*, which consists of the carbonate mixed with clay. *Blackband* is a clay ironstone, containing about 20 per cent. of carbonaceous matter. Iron also occurs very widely as *iron pyrites* FeS_2, and *copper pyrites* $CuFeS_2$, but these sulphides are not used as sources of iron.

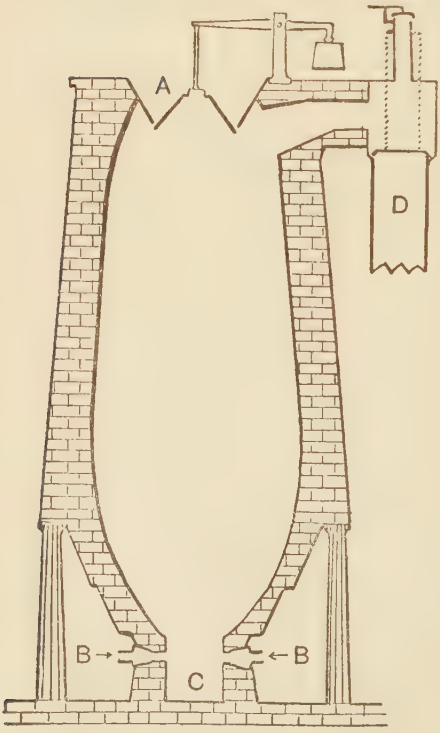

FIG. 123

Extraction — Iron is obtained from its ores

by means of a blast furnace. Fig. 123. The figure gives a general idea of a blast furnace. The ore is first heated strongly in air to drive off water and carbon dioxide, to oxidise any sulphides present, and to make the ore porous. The calcined ore is then mixed with limestone and coal, and introduced into the furnace through the cup and cone shown at **A**. A powerful hot air blast is blown in through the tuyères **B**, near the hearth **C**, and a very high temperature is produced. The hot gases obtained by the burning of the fuel and reduction of the iron oxides are carried off through **D**, and used for heating boilers or the blast. The furnace is built of a shell of iron plates, lined with firebrick to a thickness of several feet.

The following chemical reactions take place in the furnace. The oxygen of the blast forms carbon monoxide with the very hot carbon, the temperature being too high for the existence of carbon dioxide in presence of excess of carbon. The carbon monoxide reduces the hot ores to iron.

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$

In the upper part of the furnace the limestone is converted to lime and carbon dioxide, and in the hottest regions near the hearth the lime combines with the siliceous materials of the ore, forming a fusible slag, which runs down and constantly flows away through the slag hole (not shown in the figure).

The reduced iron takes up carbon, forming a fusible carbide, which melts and flows down the furnace. The carbonised iron sinks through the slag, which protects it from oxidation by the blast, and is drawn off in the liquid condition from time to time. The metal obtained is called *cast iron*. A blast furnace, 80 to 100 feet high, will turn out 1000 tons of iron per week. It may be kept in continuous action for months or years.

Cast iron or *pig iron* generally contains both combined carbon and carbon in the form of graphite. *White cast iron* contains only combined carbon. *Grey cast iron* contains both combined and graphitic carbon. Cast iron dissolves in hydrochloric acid, giving off most of its combined carbon as hydrocarbons, and leaving behind its graphitic carbon as a black powder.

Wrought iron or *malleable iron* is obtained from cast iron by the process known as *puddling*. The cast iron is melted

in an oxidising atmosphere in a reverberatory furnace, the hearth of which is lined with ferric oxide. The molten mass is stirred with iron poles until the impurities of carbon, silicon, sulphur, phosphorus, and manganese are oxidised by the air and the ferric oxide of the hearth. The impurities are evolved as gases or pass into the slag. As the iron becomes purer it grows pasty and sticks to the rods. The "bloom" of pure iron sticking to the rod is removed, and hammered to squeeze out the slag and weld the metal into a solid mass.

Steel consists of iron combined with from .15 to 1 per cent. of carbon. No graphite should be present in steel. Steel is made by several processes, of which the old cementation process and the Bessemer process are described below.

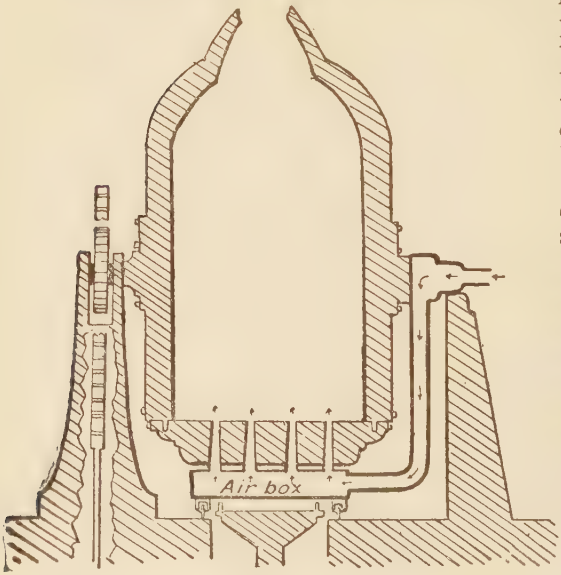

FIG. 124

Cementation process — This consists in heating bars of wrought iron to redness for some days with charcoal or carbonaceous matter. Under these conditions the bars gradually take up carbon. To ensure uniformity of composition the bars are then cut up, melted, and cast. The manner in which the carbon is conveyed into the iron is not well understood. Red hot iron has the power of absorbing 8 to 10 volumes of carbon monoxide, so that it is possible that this gas is the active agent in the introduction of the carbon. Several other possible explanations have been suggested.

The *Bessemer process* has very largely replaced the cementation process. It consists of oxidising the impurities in cast iron by blowing a blast of air through the molten metal. The operation is carried out in a large pear-shaped vessel, mounted on trunnions, and called a converter. See Fig. 124. The converter is lined with a siliceous sandstone if the cast iron contains no phosphorus, and with calcined dolomite if phosphorus is present. The oxide of phosphorus produced forms calcium and magnesium phosphates with the basic lining. Air is blown through fine openings in the bottom of the converter.

The converter is tilted into a horizontal position, molten cast iron run in, the blast is turned on, and the converter is turned back into the vertical position. The impurities are burnt away with the production of so much heat that the high-melting pure iron is kept molten. The blow is stopped when the flame at the mouth of the converter dies down. Spiegeleisen, an iron containing about 5 per cent. of carbon and from 5 to 15 per cent. of manganese, is then added to provide the necessary quantity of carbon for the production of steel. The blast is turned on for a short time to mix the materials thoroughly. The molten steel is then poured into the casting ladle, from which it is run into moulds. The whole operation, for the conversion of 10 tons of cast iron into steel, occupies about 20 minutes.

Analyses of cast iron, wrought iron, and steel

	Graphite	Combined carbon	Silicon	Sulphur	Phosphorus	Manganese	Iron
White cast iron .	—	2.40	0.80	0.70	1.50	0.20	94.4
Grey „ „ .	3.30	0.40	1.88	0.02	0.71	0.41	93.28
Wrought iron . .	—	0.15	0.14	0.04	0.47	0.14	99.13
Cementation steel	0.102	0.627	0.030	0.005	0.000	0.120	99.115
Bessemer steel .	—	0.370	Trace	0.090	0.059	0.649	98.831

Properties of cast iron, wrought iron, and steel—Cast iron is hard and brittle, and it has a tensile strength of 6 to 10

tons per square inch. Wrought iron is malleable, fibrous, and tough. Its tensile strength is about 25 tons per square inch. Steel is harder and less malleable than wrought iron, but it is fibrous and very strong. Its tensile strength varies from 30 to 60 tons per square inch. When the proportion of carbon is low, the steel is very ductile and moderately tough, and it is called *mild steel.* As the percentage of carbon increases, the steel becomes harder, more brittle, less ductile, and very tenacious. When steel is heated to temperatures varying from 220° to 300° C. and suddenly cooled, it loses its excessive hardness. This treatment is called *tempering.* Steels are thus obtained which, according to the temperature used, are suitable for different sorts of tools, etc. A stainless steel containing about ten per cent. of tungsten is now largely used for cutlery.

Properties of iron—Pure iron is a white metal. Its specific gravity is about 8. It is malleable. It melts at about 1800° C. It is attracted by a magnet, but it will not retain magnetism.

Dry air does not tarnish iron, but moist air containing carbon dioxide causes it to rust. Iron does not rust in moist air freed from carbon dioxide. Ordinary rust has the composition $2Fe_2O_3.3H_2O$. At a red heat iron decomposes steam.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

Iron is readily dissolved by dilute hydrochloric and sulphuric acids, with formation of ferrous chloride and ferrous sulphate respectively, and evolution of hydrogen.

$$Fe + 2HCl = FeCl_2 + H_2$$

With hot, strong sulphuric acid, iron forms sulphur dioxide, and a mixture of ferrous and ferric sulphates.

Cold dilute nitric acid dissolves iron, with formation of ferrous nitrate and ammonium nitrate.

$$4Fe + 10HNO_3 = 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$

With stronger nitric acid, ferric nitrate and oxides of nitrogen are obtained. Strong nitric acid of specific gravity 1.45 does not dissolve iron, but renders it *passive.* Passive iron does not dissolve in dilute nitric acid, and will not precipitate copper from solutions of copper salts. This curious condition is possibly due to the formation of a film of the magnetic oxide, Fe_3O_4, on the surface of the iron.

Iron will also combine directly with sulphur, chlorine, bromine, iodine, and oxygen.

Three oxides of iron are known, viz. ferrous oxide FeO, ferric oxide Fe_2O_3, and ferroso-ferric oxide Fe_3O_4 or $Fe_2O_3.FeO$. Ferrous and ferric oxides are basic, and give rise to ferrous and ferric salts respectively. Ferroso-ferric oxide forms with acids a mixture of ferrous and ferric salts.

Ferrous oxide, FeO (*iron monoxide, protoxide of iron*), is formed when ferrous oxalate is heated out of contact with the air. Some iron is also formed. If ferrous oxalate is added to boiling caustic potash solution, ferrous oxide is obtained as a black powder.

$$FeC_2O_4 + 2KOH = FeO + K_2C_2O_4 + H_2O$$

It is a black solid, which oxidises rapidly in air and dissolves in acids, forming ferrous salts.

Ferrous hydroxide, $Fe(OH)_2$, is obtained as a white precipitate when caustic soda solution is added to a ferrous salt. The caustic soda solution must be boiled previously to expel dissolved oxygen, and the ferrous salt must be dissolved in water, from which the air has been expelled by boiling. The hydroxide readily absorbs oxygen, and becomes first green and finally brown, owing to conversion to ferric hydroxide.

Ferric oxide, Fe_2O_3 (*sesquioxide of iron*), is obtained by heating ferric hydroxide.

$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O$$

It is a red powder, very hygroscopic, which dissolves in acids forming ferric salts. It is used, under the name of rouge, as a plate polish, and as a red paint.

Ferric hydroxide, $Fe(OH)_3$, is prepared by the addition of excess of ammonium hydroxide to solutions of ferric salts.

$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl$$

It is a brownish precipitate which readily dissolves in acids, with formation of ferric salts.

Ferroso-ferric oxide, Fe_3O_4 or $FeO.Fe_2O_3$ (*magnetic oxide of iron*), occurs in nature as *magnetite* or *loadstone*. It can be obtained by heating iron strongly in a current of steam or carbon dioxide.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$
$$3Fe + 4CO_2 = Fe_3O_4 + 4CO$$

A hydrated form of the magnetic oxide is obtained as a black precipitate when ammonium hydroxide in excess is

added to a boiling solution of a mixture of ferrous and ferric salts in the proportions indicated by the equation below.

$$FeSO_4 + Fe_2(SO_4)_3 + 8NH_4OH = FeO.Fe_2O_3.H_2O + 3H_2O + 4(NH_4)_2SO_4$$

The magnetic oxide is a black crystalline powder which is attracted by the magnet, but which does not possess the magnetic properties exhibited by loadstone. It dissolves in hydrochloric acid, forming a mixture of ferrous and ferric chlorides.

$$Fe_3O_4 + 8HCl = FeCl_2 + 2FeCl_3 + 4H_2O$$

Ferrous chloride, $FeCl_2$, is obtained in the anhydrous form in white deliquescent crystals by heating iron wire in a current of hydrochloric acid gas.

$$Fe + 2HCl = FeCl_2 + H_2$$

It is obtained as pale blue-green crystals of $FeCl_2.4H_2O$ when iron is dissolved in dilute hydrochloric acid, and the solution is crystallised.

When ferrous chloride is heated in the air it is oxidised.

$$12FeCl_2 + 3O_2 = 2Fe_2O_3 + 8FeCl_3$$

Its vapour density at high temperatures corresponds to the formula $FeCl_2$.

Ferric chloride, $FeCl_3$, is prepared in the anhydrous state by passing chlorine over heated iron wire. In solution it can be obtained by dissolving ferric oxide in strong hydrochloric acid.

Properties—The crystals of the anhydrous salt are almost black. It volatilises at high temperatures, forming a vapour, the density of which corresponds to the formula $FeCl_3$. It is deliquescent and easily soluble in water. Ferric chloride solution, when slowly evaporated, deposits yellow crystals of the composition $FeCl_3.6H_2O$.

Ferric chloride appears to be hydrolysed by water ; for, if a solution of ferric chloride, in which freshly precipitated ferric hydroxide has been dissolved, is dialysed, nearly all the chlorine is removed, and there is left a dark red liquid containing a little hydrochloric acid and much soluble ferric hydroxide. *Dialysis* is carried out by floating on water a shallow vessel, the bottom of which is made of parchment-paper or parchment. The solution to be dialysed is put into

the vessel. The water in which the dialyser floats should be frequently renewed. Substances, such as salts and acids, which can readily pass through the membrane, are called *crystalloids*. Silicic acid, soluble ferric hydroxide, and other substances which cannot pass through the parchment are called *colloids*. Soluble ferric hydroxide is therefore a colloid. Hydrochloric acid is a crystalloid.

Ferrous sulphate, $FeSO_4.7H_2O$ (*green vitriol*), is readily obtained by dissolving iron wire in dilute sulphuric acid, and evaporating the solution to the crystallising point.

$$Fe + H_2SO_4 = FeSO_4 + H_2$$

Properties—Ferrous sulphate forms pale green crystals, which effloresce on exposure to air. They are readily soluble in water. When heated to 100° C. the crystals lose six molecules of water, and $FeSO_4.H_2O$ is produced.

Ferrous sulphate is slowly oxidised by air. It forms with ammonium sulphate a double salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, which is less easily oxidised on exposure to air than ferrous sulphate itself. Ferrous sulphate, like all ferrous salts, is readily oxidised by potassium permanganate or bichromate in presence of sulphuric acid.

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

A cold saturated solution of ferrous sulphate dissolves nitric oxide, giving a brown solution, which contains the compound $FeSO_4.NO$. When the solution is warmed, pure nitric oxide is evolved.

Ferrous sulphate is used for the preparation of inks, iron mordants, Prussian blue, etc.

Ferric sulphate, $Fe_2(SO_4)_3$, is prepared by oxidising ferrous sulphate solution with nitric acid in the presence of sulphuric acid.

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 2NO + 4H_2O + 3Fe_2(SO_4)_3$$

On evaporation the ferric sulphate is obtained as a white mass. It is not very soluble in water. It forms alums with the sulphates of potassium, sodium, and ammonium, *e.g.* iron alum, $K_2SO_4.Fe_2(SO_4)_3.24H_2O$.

Ferrous sulphide, **FeS**, is made by throwing a mixture of fine iron filings and sulphur into a red-hot crucible. Much

heat is given out as combination takes place. It can also be obtained by adding ammonium sulphide to solutions of ferrous or ferric salts. It is precipitated as a black amorphous powder.

$$FeCl_2 + (NH_4)_2S = FeS + 2NH_4Cl$$
$$2FeCl_3 + 3(NH_4)_2S = 2FeS + 6NH_4Cl + S$$

Ferrous sulphide is used for the preparation of sulphuretted hydrogen.

$$FeS + H_2SO_4 = FeSO_4 + H_2S$$

Other sulphides of iron, Fe_2S_3, FeS_2 (iron pyrites), Fe_3S_4 (magnetic pyrites), are also known.

Tests for iron—

(1) Ammonium hydroxide gives a dirty green precipitate of ferrous hydroxide, $Fe(OH)_2$, with ferrous salts, and a brownish-red precipitate of ferric hydroxide, $Fe(OH)_3$, with ferric salts.

(2) Potassium ferrocyanide gives with ferrous salts a white precipitate of $K_2Fe_2(CN)_6$, which rapidly becomes blue by oxidation ; with ferric salts it gives a deep blue precipitate of Prussian blue, $Fe_7(CN)_{18}$.

$$4FeCl_3 + 3K_4Fe(CN)_6 = Fe_7(CN)_{18} + 12KCl$$

(3) Potassium ferricyanide gives a deep blue precipitate of Turnbull's blue, $Fe_5(CN)_{12}$, with ferrous salts, and a reddish-brown coloration with ferric salts.

$$3FeCl_2 + 2K_3Fe(CN)_6 = Fe_5(CN)_{12} + 6KCl$$

(4) Potassium sulphocyanate gives a deep red coloration of ferric sulphocyanate, $Fe(CNS)_3$, with ferric salts, but no coloration with ferrous salts.

(5) Ferrous and ferric salts fused with borax in the oxidising flame give yellowish-red beads, and in the reducing flame green beads.

CHAPTER XL

ALUMINIUM AND ITS COMMON COMPOUNDS

Exp. 208—To observe some of the properties of aluminium

Directions—

(1) Notice the colour, lustre, and hardness of aluminium.

(2) Find out if the metal is soluble in dilute sulphuric acid, dilute nitric acid, dilute hydrochloric acid, and a fairly strong

solution of caustic soda. In each case identify any gaseous products.

(3) Dissolve one or two crystals of nitre in caustic soda, add a small piece of aluminium, and warm gently. Identify the gaseous product, and explain its formation.

Exp. 209—To test for aluminium

Directions—

(1) To a solution of an aluminium salt add ammonium chloride solution and ammonia.

(2) To a solution of an aluminium salt add a few drops of caustic soda. Afterwards add excess of caustic soda and warm the liquid.

(3) Heat a small quantity of a solid aluminium compound on charcoal before the blow-pipe, moisten the resulting mass with cobalt nitrate solution, and reheat.

Exercises—

(1) Prepare aluminium oxide from potash alum.

(2) Prepare a specimen of crystalline aluminium chloride from the metal.

ALUMINIUM, Al=27

Aluminium is very abundant in nature. As oxide, Al_2O_3, it occurs as *ruby, sapphire, emery,* and *corundum* ; as hydrated oxide, $Al_2O_3.H_2O$, it is found combined with iron oxide in *bauxite* ; as silicate in the *clays* and *felspars* ; and as a double fluoride of aluminium and sodium in *cryolite*, $AlF_3.3NaF$.

The metal is prepared on the large scale by electrolysing between carbon electrodes aluminium oxide dissolved in molten cryolite. It can also be obtained by electrolysis of fused alumina.

Properties—Aluminium is nearly as white as silver. It is about as hard as zinc. It has a specific gravity of only 2.6. It has great tensile strength, and it is malleable and ductile. Air at ordinary temperatures does not tarnish it, but it burns in air when heated strongly in the form of thin sheet. It melts at about 700° C.

The metal dissolves readily in hydrochloric acid and in caustic soda solution, hydrogen being set free in each case. Thus :—

$$2Al + 6HCl = 2AlCl_3 + 3H_2$$

$$2Al + 6NaOH = 2Al(ONa)_3 + 3H_2$$

Sodium aluminate

Aluminium reacts with hot strong sulphuric acid, forming aluminium sulphate and setting free sulphur dioxide.

Aluminium forms a very tenacious alloy with one-tenth of its weight of copper. This alloy is known as *aluminium bronze* or *aluminium gold*. Its colour resembles that of gold; air hardly tarnishes it; and it takes a high polish. Aluminium bronze is used for making cheap ornaments, and for a number of other purposes.

Aluminium oxide (*alumina*), Al_2O_3, is obtained as an amorphous white powder, when ammonia is added to a solution of an aluminium salt, and the washed precipitate is ignited.

$$AlCl_3 + 3NH_4OH = Al(OH)_3 + 3NH_4Cl$$
$$2Al(OH)_3 = Al_2O_3 + 3H_2O$$

It can also be prepared by heating ammonia alum strongly, when alumina is left in an amorphous condition.

It is a soft white powder, which is soluble in acids, if it has not been strongly heated, but very insoluble if it has been heated strongly. The natural crystalline forms, ruby, sapphire, emery, and corundum are nearly as hard as diamond.

Aluminium hydroxide, $Al(OH)_3$, falls as a gelatinous precipitate when ammonia is added to a solution of an aluminium salt. If the precipitate is dried at 100° C., it has the composition $Al(OH)_3$, but if it is heated more strongly, hydrated oxides are obtained.

Aluminium hydroxide is soluble in acids, and in caustic alkalis. With caustic potash the reaction is:—

$$Al(OH)_3 + 3KOH = \underbrace{Al(OK)_3}_{\text{Potassium aluminate}} + 3H_2O$$

If aluminium hydroxide is precipitated in solutions containing certain organic colouring matters, the hydroxide carries down with it the colouring matter in the form of a *lake*. Its attraction for colouring matters renders it valuable as a *mordant*. If such a lake is precipitated within the fibres of cotton goods, the colouring matter is held fast in the fabric by the *mordant*, *i.e.* by the aluminium hydroxide, and the colour does not "run" when the fabric is washed.

Aluminium chloride, $AlCl_3$, is usually prepared by passing

chlorine over an intimate mixture of carbon and alumina heated strongly, in an earthenware retort.

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO$$

The hydrated chloride can be obtained by dissolving aluminium in hydrochloric acid, and evaporating the solution until crystals of $AlCl_3.6H_2O$ are deposited.

The anhydrous chloride is a white crystalline solid, which fumes strongly in moist air. It can be vaporised without fusion or decomposition. It dissolves in water with evolution of heat. Crystals of the hydrated chloride can be obtained from the solution.

The hydrated chloride breaks up, on heating, into hydrochloric acid, alumina and water.

$$2AlCl_3.6H_2O = Al_2O_3 + 9H_2O + 6HCl$$

Aluminium chloride forms double salts with other chlorides, *e.g.*, $AlCl_3.NaCl$.

Aluminium sulphate, $Al_2(SO_4)_3.18H_2O$, is obtained as a soluble white salt when aluminium hydroxide is dissolved in dilute sulphuric acid and the solution is evaporated. It is used chiefly for making alums.

Potash alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, is prepared by mixing in solution the calculated quantities of the two sulphates, and crystallising the resulting solution.

Properties—Alum is a colourless solid, which crystallises in regular octahedra. On exposure to air the crystals become coated with a white basic salt, due to the absorption of atmospheric ammonia by the alum. The solubility of alum at 0° C. is 4, and at 100° C. it is 357.

When heated, alum melts in its water of crystallisation, then gives off the water, and becomes converted into a porous white mass of *burnt alum*. This dissolves in water very slowly. Heated more strongly, alum splits up into potassium sulphate, alumina, and sulphur trioxide.

Ammonia precipitates aluminium hydroxide from solutions of potash alum.

The alums—Many other alums exist. All the alums are isomorphous with one another. They crystallise in octahedra or cubes belonging to the regular system. All are double sulphates containing 24 molecules of water of crystallisation in a molecule of the double salt. They have the general formula $R'_2SO_4.R'''_2(SO_4)_3.24H_2O$, where R′ represents a

monad metal such as sodium, potassium, or ammonium, and R''' represents a triad metal such as aluminium, chromium, manganese, or iron.

Tests for aluminium—

(1) Solutions of aluminium salts give with ammonium chloride and ammonia a white gelatinous precipitate of aluminium hydroxide.

(2) Caustic soda precipitates aluminium hydroxide from solutions of aluminium salts. The hydroxide is soluble in excess of the caustic soda, sodium aluminate, $Al(ONa)_3$, being formed.

(3) When a solid aluminium compound is heated on charcoal, and then moistened with cobalt nitrate solution and reheated, an infusible blue mass is obtained.

CHAPTER XLI

MANGANESE AND ITS COMMON COMPOUNDS

Exp. 210—To prepare potassium permanganate and observe some of its properties

Directions—Into an iron crucible put about 20 grams of caustic potash with about 40 c.c. of water. Warm until the potash has dissolved. Next, mix with the liquid about 20 grams of manganese dioxide, and about 10 grams of potassium chlorate. Evaporate to dryness and heat strongly. Allow to cool. Dissolve out the soluble product with water, and filter the liquid through asbestos. Through the green solution of potassium manganate pass carbon dioxide until the colour changes to purple. Concentrate the solution until potassium permanganate crystalliises out on cooling.

Carry out the following experiments with a solution of your potassium permanganate :—

(1) Pass sulphuretted hydrogen through the acidified solution.

(2) Pass sulphur dioxide through the solution acidified with sulphuric acid.

(3) Acidify the solution with sulphuric acid and warm with a few c.c. of oxalic acid solution.

(4) Acidify the solution and add a few c.c. of hydrogen peroxide solution.

In each case note colour changes, nature of the gases evolved, if any, and the nature of any precipitate which may be formed. Try to represent the reactions by equations.

Exp. 211—To test for manganese

Directions—

(1) To a solution of a manganese salt add first ammonium chloride, then ammonia, and finally ammonium sulphide solution.

(2) To a solution of a manganese salt add caustic soda. Notice any change in the colour of the precipitate on standing.

(3) Heat a small quantity of borax in a loop of platinum wire until a clear bead is obtained. Dip this bead into a small quantity of a manganese salt, and heat again.

(4) Fuse a manganese compound with sodium carbonate and a crystal of potassium nitrate on platinum foil. Notice the colour of the product.

Exercises—Prepare specimens of manganese chloride and sulphate from manganese dioxide.

MANGANESE, Mn=55

Manganese does not occur in the free state in nature, but in combination with oxygen it is found widely as *pyrolusite*, MnO_2, as *braunite*, Mn_2O_3, and as *hausmannite*, Mn_3O_4. It also occurs as *manganese spar*, $MnCO_3$.

The metal can be obtained by reducing the oxide by carbon at a high temperature. It is a steel-grey metal, hard and brittle. Its specific gravity is 7.4. It is oxidised rapidly by moist air, and it dissolves readily in dilute hydrochloric acid or sulphuric acid, forming manganous salts and setting free hydrogen.

Manganese oxide, MnO, can be prepared by heating one of the higher oxides in a stream of hydrogen. It is a greenish powder, which is rapidly oxidised on exposure to air. It is a basic oxide which dissolves in acids, producing manganous salts.

Manganous hydroxide, $Mn(OH)_2$, can be obtained as a

white precipitate if solutions of caustic soda and manganous sulphate, which have been boiled to free them from air, are mixed together.

$$MnSO_4 + 2NaOH = Mn(OH)_2 + Na_2SO_4$$

The white precipitate rapidly turns brown owing to oxidation by the air. Manganous oxide and hydroxide resemble ferrous oxide and hydroxide in the ease with which they are oxidised.

Mangano-manganic oxide, Mn_3O_4, is a basic peroxide, which occurs native as the mineral *hausmannite*. It is a red solid.

Manganic oxide (*manganese sesquioxide*), Mn_2O_3, occurs in nature as *braunite*. It is said to be formed when manganous hydroxide is heated gently. It is a basic peroxide. A hydrated oxide of the formula, $Mn_2O_3.H_2O$, occurs native as the mineral *manganite*.

Manganese dioxide, MnO_2, occurs native as *pyrolusite*. It is obtained when manganese nitrate is heated carefully.

$$Mn(NO_3)_2 = 2NO_2 + MnO_2$$

It is also obtained in the hydrated form when bleaching powder solution is added to a solution of manganese sulphate made alkaline with caustic soda.

$$MnO.H_2O + CaOCl_2 = MnO_2.H_2O + CaCl_2$$

It is a black solid, which loses oxygen when heated strongly.

$$3MnO_2 = Mn_3O_4 + O_2$$

It is a basic peroxide. When heated with strong hydrochloric acid, it sets free chlorine, and when heated with strong sulphuric acid it gives off oxygen. Thus :—

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$$

It is used in the preparation of oxygen from potassium chlorate, and in the preparation of chlorine on the large scale in Weldon's process.

Manganous chloride, $MnCl_2$, can be obtained by dissolving manganese carbonate, or any of the oxides of manganese in hydrochloric acid. It crystallises from solution in pink crystals, which have formula $MnCl_2.4H_2O$. The anhydrous salt has no colour.

Manganic chloride, $MnCl_3$ or $MnCl_4$, probably exists in the brown solution obtained by dissolving manganese dioxide in cold strong hydrochloric acid. It has not been isolated.

Manganous sulphate, $MnSO_4$, is prepared by heating manganese dioxide with strong sulphuric acid, dissolving out the salt from the residue with water, and evaporating the solution to the crystallising point. Large pink crystals of the composition $MnSO_4.5H_2O$ are obtained. These crystals are isomorphous with copper sulphate. If the solution is crystallised at temperatures below 6° C., the crystals deposited have the composition $MnSO_4.7H_2O$, and are isomorphous with ferrous sulphate, $FeSO_4.7H_2O$.

If hydrated manganous sulphate is heated to 200° C., the anhydrous salt is obtained.

Manganic sulphate, $Mn(SO_4)_3$, is obtained as a green powder when precipitated manganese dioxide is treated with sulphuric acid. It decomposes partially on exposure to air into sulphuric acid and hydrated manganic oxide, $Mn_2O_3.H_2O$. If potassium sulphate solution be added to a solution of manganic sulphate in dilute sulphuric acid, crystals of potassium manganese alum, $K_2SO_4.Mn_2(SO_4)_3.24H_2O$, separate out. The alum crystallises in violet octahedra, which are decomposed by excess of water with separation of the hydrated manganic oxide.

Manganates and permanganates—In the above salts manganese is acting as an electro-positive element. In manganates and permanganates it forms part of an electro-negative group.

The *manganates* of the alkali metals are obtained by fusing together manganese dioxide, caustic potash or soda, and potassium nitrate or chlorate. The nitrate or chlorate provide oxygen.

$$MnO_2 + 2KOH + O = K_2MnO_4 + H_2O$$

The resulting mass is green. It dissolves to a green solution, which is stable in presence of alkali. If the solution is diluted largely, or if the alkali is neutralised with carbon dioxide, or acid, the manganate changes to *permanganate*, and the colour of the solution, consequently, alters to purple or pink. Thus—

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH$$
$$3K_2MnO_4 + 2CO_2 = 2KMnO_4 + MnO_2 + 2K_2CO_3$$

The manganates may be regarded as derived from the hypothetical acid, H_2MnO_4. The acidic oxide, MnO_3, corresponding to this acid, is known. In the preparation of

the manganates from manganese dioxide, the valency of the manganese has been increased from four to six. The change is, therefore, a good example of an oxidation.

Permanganates may in a similar way be regarded as derived from the hypothetical acid, $HMnO_4$, corresponding to the unstable heptoxide, Mn_2O_7. In permanganates, therefore, manganese has a valency of seven.

Potassium permanganate, $KMnO_4$, is prepared in the manner described in Exp. 210. If the solution is filtered through filter paper, hydrated oxides of manganese come down on evaporation. The potassium permanganate is reduced by the organic matter which it has extracted from the filter paper.

The salt crystallises in purple prisms, which are isomorphous with crystals of potassium perchlorate. The solubility of the salt at ordinary temperatures is about 7.

Potassium permanganate readily gives up its oxygen. If heated to 240° C., it decomposes.

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$

Among its oxidising reactions are the following :—

$$2KMnO_4 + 5H_2S + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5S + 8H_2O$$

$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O$$

It will be seen that in each case the permanganate gives up 5 of its oxygen molecules for oxidising purposes. The permanganate may therefore be regarded as $K_2O.2MnO.5O$. The acid present takes up the K_2O and MnO, and the five oxygen atoms are free to oxidise. In each case the permanganate is decolorised, since the manganese sulphate solution is practically colourless.

Sodium permanganate is used largely as a disinfectant under the name of Condy's Fluid.

Tests for manganese—

(1) A hydrated pink form of manganese sulphide is precipitated when ammonium chloride, ammonia, and ammonium sulphide are added to a solution of a manganese salt.

(2) Caustic soda precipitates from solutions of manganese

salts a white precipitate of manganous hydroxide, which darkens immediately owing to oxidation by the air.

(3) The manganese borax bead is colourless in the reducing flame, and violet in the oxidising flame.

(4) When a solid manganese compound is fused on platinum foil with sodium carbonate and potassium nitrate, a green mass of potassium manganate is formed.

Comparison of iron, aluminium, and manganese—The metals are not much alike in physical properties. Iron, when pure, is hard and malleable, aluminium is soft, and malleable, and manganese is hard and brittle. Iron is white, aluminium is silver white, and manganese is grey.

Aluminium differs from the others in being unattacked by nitric acid, but all three metals behave in a similar way towards sulphuric acid and hydrochloric acid. Aluminium forms only one oxide, iron forms three, and manganese six. Aluminium forms only one series of salts in which it is tribasic; iron forms ferrous salts in which it is dibasic, and ferric salts in which it is tribasic; and manganese forms manganous salts in which it is dibasic, and manganic salts in which it is tribasic. The ferric salts are more stable than the ferrous salts, but the manganous salts are more stable than the manganic salts.

All three metals can form part of electro-negative groups. Thus, aluminium forms aluminates, *e.g.*, sodium aluminate, Na_3AlO_3. Iron forms ferrates, *e.g.*, potassium ferrate, K_2FeO_4, and manganese forms manganates and permanganates, *e.g.*, the potassium salts K_2MnO_4 and $KMnO_4$. Of these salts the only stable ones are the permanganates. It would appear, therefore, that the metals are not very closely allied, that is, the metals do not resemble one another so closely that they should be classed in the same sub-group of the Periodic Classification.

CHAPTER XLII

LEAD AND ITS COMMON COMPOUNDS

Exp. 212—To observe some of the reactions of lead salts

Directions—Carry out the following tests with solutions of lead salts :—

(1) Add hydrochloric acid. Warm the precipitate with excess of water, and allow to cool.

(2) Add dilute sulphuric acid.

(3) Add potassium iodide solution. Warm the precipitate with excess of water, and allow to cool.

(4) Add potassium chromate solution.

(5) Heat a mixture of a solid lead salt and sodium carbonate on charcoal before the blow-pipe. Note the colour of the incrustation, and the hardness and solubility in acids of the metallic bead formed.

Exp. 213—To prepare lead monoxide and lead peroxide

Directions—

(1) Make lead monoxide by heating lead carbonate or nitrate to low redness.

(2) Make lead peroxide by treating red lead with dilute nitric acid. Filter; wash and dry the oxide.

(3) Make lead peroxide from lead nitrate, caustic soda, and bleaching powder. See bleaching powder, page 360. Use excess of bleaching powder solution. Warm the mixed solutions until the colour of the precipitate is dark brown. Wash by decantation.

Exercises—Prepare specimens, crystalline if possible, of lead nitrate, lead chloride, lead iodide, and lead sulphate from lead monoxide.

LEAD, Pb. Atomic weight=207

Occurrence—The chief ores of lead are *galena*, PbS, and *cerussite*, $PbCO_3$. *Anglesite*, $PbSO_4$, is less common.

Extraction—Lead is obtained from its ores by self-reduction. The ores are roasted in a reverberatory furnace to convert them partially to lead oxides and sulphate. The temperature is then raised to enable the oxides, sulphate, and sulphide to react. The main reactions taking place are—

$PbS + 2O_2 = PbSO_4$ $\qquad$ $2PbS + 3O_2 = 2PbO + 2SO_2$

$PbS + PbSO_4 = 2Pb + 2SO_2$ $\qquad$ $PbS + 2PbO = 3Pb + SO_2$

Lead is also obtained by smelting the ores in a blast furnace with metallic iron, or with materials which will produce metallic iron when heated in the furnace.

$$PbS + Fe = FeS + Pb$$

The iron sulphide, together with other metallic sulphides, rises to the top of the molten lead as a matter.

The lead obtained by these processes may contain silver,

antimony, tin, copper, and iron. These impurities, which make the lead hard, are removed by heating the metal in a reverberatory furnace. Most of the metallic impurities are oxidised. The oxides rise to the surface as a dross, which is removed. Silver is not removed.

Desilverisation of lead—Silver in lead is now removed and recovered by Pattinson's process. This process depends on the fact that, when molten lead containing silver is allowed to cool, the crystals which separate are almost pure lead. The silver-lead alloy is melted in a large iron pot, which forms one of a series. As the pot cools the lead crystals are removed with a perforated ladle and placed in the next pot until seven-eighths of the contents of the first pot have been removed. The residue of silver-lead alloy is put into the next pot on the other side, and a new charge is worked up in the first vessel. The contents of the neighbouring pots are treated in the same way, with the result that lead, almost free from silver, collects at one end of the series, and a rich silver lead alloy at the other end. The silver-lead alloy is *cupelled*, that is, it is heated strongly in an oxidising atmosphere until all the lead has been removed as lead monoxide (litharge), and a glowing mass of molten silver is left.

Properties—Lead is a soft, bluish-white metal, which, when freshly cut, has a bright metallic lustre. Its surface is oxidised by air. Its specific gravity is 11.3. It melts at 330° C., and when heated strongly in air it is oxidised to the monoxide, PbO.

Nitric acid dissolves the metal readily with formation of lead nitrate and oxides of nitrogen. Cold hydrochloric acid and cold sulphuric acid have little effect on lead, but hot strong hydrochloric acid converts it slowly to lead chloride with evolution of hydrogen, and hot strong sulphuric acid converts it to lead sulphate with evolution of sulphur dioxide.

Pure water has no action on lead, but water containing dissolved air and carbon dioxide, or water containing in solution chlorides, nitrates or ammonium salts, has a solvent action. Lead is a cumulative poison, so that very small quantities of lead in drinking water are dangerous. Since drinking water is frequently stored in leaden cisterns and is supplied through leaden pipes, it should be free from chlorides, nitrates and ammonium salts.

There are three common oxides of lead, viz. lead monoxide PbO, red lead Pb_3O_4, and lead peroxide PbO_2.

Lead monoxide, PbO (*Litharge, massicot*), is made by heating the metal strongly in air, or by heating the carbonate or nitrate.

Properties—It is a heavy solid, yellow to reddish in colour. It is slightly soluble in water. The solution has an alkaline reaction with litmus. It is a basic oxide. It readily dissolves in acids to form salts. It is used for making flint glass, as a glaze for pottery, and for the preparation of other compounds of lead.

A hydrated oxide of lead, $2PbO+H_2O$, is precipitated when ammonium hydroxide or caustic soda is added to a solution of lead acetate.

Red lead, Pb_3O_4 (*Minium, tri-plumbic tetroxide*), is obtained when lead monoxide, or lead carbonate is heated in air for a long time to a temperature of 450° C.

Properties—It is a scarlet, crystalline powder, which becomes darker when heated, and regains its original colour on cooling. Heated more strongly, it gives off oxygen and forms the monoxide.

$$2Pb_3O_4=6PbO+O_2$$

The reaction of red lead with dilute nitric acid points to a composition $PbO_2.2PbO$ for the oxide.

$$PbO_2.2PbO+4HNO_3=2Pb(NO_3)_2+PbO_2+2H_2O$$

Red lead is used as a pigment, and in the manufacture of flint glass.

Lead peroxide, PbO_2, is obtained as a dark brown powder by treating red lead with dilute nitric acid. It is also formed when a solution of a lead salt, made alkaline with caustic soda solution, is treated with chlorine or with excess of bleaching powder solution.

$$2Pb(NO_3)_2+4NaOH=(PbO)_2.H_2O+4NaNO_3+H_2O$$
$$(PbO)_2.H_2O+2CaOCl_2=2PbO_2+2CaCl_2+H_2O$$

Properties—It is a brown solid, which gives up part of its oxygen when heated.

$$2PbO_2=2PbO+O_2$$

Lead peroxide is a powerful oxidising agent. A mixture of lead peroxide and flowers of sulphur inflames when rubbed in a mortar. If sulphur dioxide is passed over dry lead

peroxide, lead sulphate is produced, with evolution of so much heat that the product becomes red hot.

$$PbO_2 + SO_2 = PbSO_4$$

When it is heated with strong hydrochloric acid, chlorine is evolved.

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$$

It evolves oxygen when heated with strong sulphuric acid.

$$2PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O + O_2$$

Fused with caustic potash, it forms potassium plumbate, K_2PbO_3.

In this reaction it acts like an acid-forming oxide.

Other oxides of lead are known, viz. *lead suboxide*, Pb_2O, obtained as a grey powder by heating lead oxalate out of contact with the air, and *lead sesquioxide*, Pb_2O_3, obtained as a yellow powder by adding sodium hypochlorite solution to a solution of lead monoxide in caustic soda solution.

Lead chloride, $PbCl_2$, is obtained as a curdy white precipitate when hydrochloric acid, or a solution of a chloride, is added to a solution of a lead salt.

$$Pb(NO_3)_2 + 2NaCl = PbCl_2 + 2NaNO_3$$

The precipitate dissolves in hot water, and gives a solution which deposits sharp needle-shaped crystals of lead chloride on cooling. It is only slightly soluble in cold water.

Lead tetrachloride, $PbCl_4$, is obtained in solution when lead peroxide is dissolved in cold, strong hydrochloric acid. The salt is unstable, and its solution gives lead chloride and chlorine when warmed.

$$PbCl_4 = PbCl_2 + Cl_2$$

Lead nitrate, $Pb(NO_3)_2$, is obtained by dissolving metallic lead, or the monoxide, or carbonate, in nitric acid and evaporating the solution.

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O$$

It is a white, crystalline salt, which is soluble in water. When heated it decomposes.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

Lead sulphate, $PbSO_4$, is obtained as a white insoluble precipitate when dilute sulphuric acid, or a soluble sulphate, is added to a solution of a lead salt.

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3$$

Lead sulphate is practically insoluble in water, but it

dissolves readily in strong sulphuric acid, and in solutions of ammonium salts or caustic alkalis.

Lead sulphide, **PbS,** is obtained as a black precipitate when sulphuretted hydrogen is passed through a solution of a lead salt.

$$Pb(NO_3)_2 + H_2S = PbS + 2HNO_3$$

Lead sulphide is insoluble in cold dilute acids, but soluble in hot dilute nitric acid.

Basic lead carbonate, $Pb(OH)_2.2PbCO_3$ (*white lead*), is made on the large scale for use as a white paint. The best white lead is prepared by the *Dutch process*. Rough gratings of lead, or coils of sheet lead, are placed in earthenware pots, Fig. 125, containing a small quantity of vinegar. The pots are placed in a shed on a thick bed of spent tan bark or stable manure. They are then covered with planks spread with manure, and a second row of pots is placed on the planks. More pots are added until the shed is completely filled. The shed is then left undisturbed for three months. The tan bark, etc., ferments, and produces heat and carbon dioxide. The acetic acid vapour from the vinegar, together with the oxygen of the air, produces basic lead acetate. This salt reacts with the carbon dioxide, and forms white lead and normal lead acetate. The lead acetate, in the presence of air and moisture, combines with more lead and forms again the basic acetate. So the process goes on until most of the lead has been converted into white lead. The reactions may be expressed by the equations :—

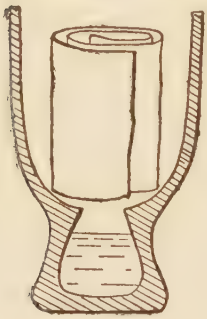

FIG. 125

$$2CH_3.COOH + 2Pb + O_2 = (CH_3.COO)_2Pb.Pb(OH)_2$$

Acetic acid — Basic lead acetate

$$3\{(CH_3.COO)_2Pb.Pb(OH)_2\} + 2CO_2 = 3(CH_3COO)_2Pb + Pb(OH)_2.2PbCO_3 + 2H_2O$$

Normal lead acetate — White lead

$$2(CH_3.COO)_2Pb + 2Pb + O_2 + 2H_2O = 2\{(CH_3.COO)_2Pb.Pb(OH)_2\}$$

Basic lead acetate

Tests for lead—

(1) Hydrcohloric acid precipitates lead chloride, $PbCl_2$, from solutions of lead salts, as a white precipitate, soluble in hot water.

(2) Dilute sulphuric acid gives a white, insoluble precipitate of lead sulphate, $PbSO_4$, soluble in caustic soda.

(3) Potassium iodide gives a yellow precipitate of lead iodide, PbI_2, soluble in hot water. The solution on cooling deposits golden yellow spangles of lead iodide.

(4) Potassium chromate gives a bright yellow precipitate of lead chromate, $PbCrO_4$, soluble in caustic soda.

(5) Lead salts, heated with sodium carbonate on charcoal before the blow-pipe, yield malleable beads of metallic lead, and form a yellow crust of lead monoxide on the charcoal. The beads mark paper and dissolve in nitric acid.

CHAPTER XLIII

TIN AND ITS COMMON COMPOUNDS

Exp. 214—To observe the reactions of tin salts with some reagents

Directions—Carry out the following tests with solutions of stannous and stannic salts :—

(1) Pass sulphuretted hydrogen, pour off the liquid from the precipitate, and warm the precipitate with ammonium sulphide solution. When a clear solution is obtained, add excess of dilute hydrochloric acid.

(2) Add a few drops of caustic soda solution, and afterwards heat the precipitate with excess of the reagent.

(3) Add a few drops of mercuric chloride solution and warm.

(4) Add a piece of metallic zinc, and allow to stand for a short time.

(5) Boil a stannic salt with metallic copper and hydrochloric acid. Afterwards test the solution with a few drops of mercuric chloride.

(6) Mix a solid tin compound with potassium cyanide, and heat the mixture on charcoal with the blow-pipe. Test the malleability, hardness, and solubility of the bead obtained.

Exercises—Prepare the following compounds of tin :—

(1) Stannous oxide. Heat stannous oxalate in a hard glass tube.

(2) Stannic oxide. Warm metallic tin with excess of strong nitric acid, evaporate to dryness, and strongly ignite the residue.

(3) Stannous chloride. Dissolve tin in strong hydrochloric acid and evaporate until the solution crystallises on cooling.

(4) Stannic chloride. Pass dry chlorine over metallic tin, heated in a tubulated retort, and collect the liquid distillate in a well-cooled flask. See Fig. 126.

TIN, Sn. Atomic weight = 118

Occurrence—Tin occurs in large quantities in a few localities as the oxide, SnO_2, in the form of *tinstone* or *cassiterite*. It is sometimes found in streams in nodules of pure oxide known as *stream tin*. These nodules, owing to their high specific gravity, are not carried away by the water.

Extraction—The ores are sorted, broken up, washed, and roasted in air to drive off sulphur and arsenic as sulphur dioxide and arsenious oxide respectively. The arsenious oxide is collected in condensing flues. The calcined ore is washed to remove the copper sulphate formed in the roasting, and to wash away iron oxide and other light impurities. It is next mixed with powdered anthracite, and heated in a reverberatory furnace.

$$SnO_2 + 2C = Sn + 2CO$$

The metal obtained is purified by melting on the sloping hearth of a furnace, when the easily fusible tin melts and runs away from the less fusible impurities. This process is called *liquation*. The tin is finally purified by stirring the molten metal with poles or billets of green wood. The impurities separate as a scum or dross, which can readily be removed.

Properties—Tin is a bright, white, crystalline metal, which is sufficiently soft to be cut with a knife. It melts at 227° C. It is very brittle at temperatures near its melting-point.

If a bar of tin be bent quickly backwards and forwards several times it emits a slight grating sound, and becomes hot from the friction of the crystalline particles on one another.

Tin is not affected by the air, and it is not corroded by vegetable acids. It is therefore very useful for coating sheet iron and metallic cooking vessels. *Tin plate* is sheet iron, coated with tin by dipping the thoroughly cleansed iron into molten tin.

When strongly heated in the air, tin burns, forming stannic oxide, SnO_2.

Tin reacts with hot strong sulphuric acid, forming stannous sulphate and sulphur dioxide.

$$Sn + 2H_2SO_4 = SnSO_4 + 2H_2O + SO_2$$

It dissolves in strong hydrochloric acid, forming stannous chloride and hydrogen.

$$Sn + 2HCl = SnCl_2 + H_2$$

The strongest nitric acid does not attack tin, but ordinary strong nitric acid attacks it violently, forming metastannic acid and nitrogen peroxide.

$$5Sn + 20HNO_3 = H_{10}Sn_5O_{15} + 20NO_2 + 5H_2O$$

Stannous oxide, SnO, is obtained as a black solid when stannous oxalate is heated out of contact with the air.

$$SnC_2O_4 = SnO + CO + CO_2$$

When the oxide is heated in the air, it is converted to the dioxide with incandescence. It is a basic oxide which dissolves in acids, forming stannous salts.

Stannic oxide, SnO_2, is formed when the metal is burnt in air. It is most readily prepared by ignition of metastannic acid, which is obtained by the action of strong nitric acid on tin.

$$H_{10}Sn_5O_{15} = 5H_2O + 5SnO_2$$

Properties—Stannic oxide is a white powder, which changes to yellow and brown on heating, but regains its original colour on cooling. It is not acted upon by acids or solutions of alkalis, but, when fused with caustic potash, it is converted into potassium stannate.

$$2KOH + SnO_2 = K_2SnO_3 + H_2O$$

Stannous chloride, $SnCl_2$, is obtained as the anhydrous salt by heating tin filings with mercuric chloride. The mercury volatilises and leaves stannous chloride.

$$Sn + HgCl_2 = SnCl_2 + Hg$$

The hydrated salt, $SnCl_2.2H_2O$, is obtained when tin is dissolved in strong hydrochloric acid, and the solution obtained is evaporated until crystals separate on cooling.

Properties—Stannous chloride is a white solid, which boils at 600°, giving a vapour of which the density corresponds to the formula $SnCl_2$.

Stannous chloride is soluble in a small quantity of water. With excess of water it forms an insoluble basic chloride.

$$2SnCl_2 + 2H_2O = SnCl_2.Sn(OH)_2 + 2HCl$$

Dilute hydrochloric acid is therefore generally used as a solvent for stannous chloride.

The solution has powerful reducing properties. It reduces

mercuric chloride solution to mercurous chloride, and, on boiling, to metallic mercury.

$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl$$
$$SnCl_2 + 2HgCl = SnCl_4 + 2Hg$$

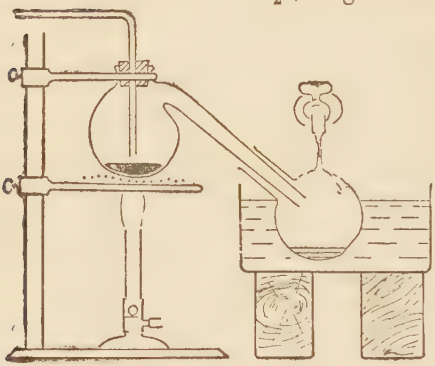

FIG. 126

Stannic chloride, $SnCl_4$, is obtained by passing a stream of dry chlorine over tin melted in a retort. The chloride is collected in a well-cooled dry receiver. See Fig. 126.

$$Sn + 2Cl_2 = SnCl_4$$

Properties — Stannic chloride is a colourless mobile liquid which boils at 114° C. It fumes strongly in air. It unites with water, forming hydrated salts of the composition $SnCl_4.3H_2O$, $SnCl_4.5H_2O$, and $SnCl_4.8H_2O$. The salt $SnCl_4.5H_2O$ is used as a mordant* under the name *oxymuriate of tin.*

Stannous sulphide, SnS, is obtained as a lead-coloured mass when tin foil is burnt in sulphur vapour. It is obtained as a brown precipitate of the hydrated sulphide when sulphuretted hydrogen is passed through a solution of a stannous salt. When this precipitate is dried, it becomes black and anhydrous. Stannous sulphide is converted by ammonium sulphide solution into stannic sulphide, which dissolves, forming ammonium thiostannate.

$$SnS + S = SnS_2 \quad \text{(From the ammonium sulphide)}$$

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3 \quad \text{Ammonium thiostannate}$$

Stannic sulphide, SnS_2, is obtained as *mosaic gold* by heating tin amalgam, sulphur, and ammonium chloride in a retort. Stannic sulphide is left behind as a mass of golden scales. The sulphide is obtained as a yellow precipitate when sulphuretted hydrogen is passed through a solution of a stannic salt.

* A *mordant* is a substance used in dyeing to fix the dye in the fibre of the cloth.

Mosaic gold is used as a pigment.

Tests for tin—

(1) Sulphuretted hydrogen precipitates brown stannous sulphide, SnS, from stannous salts, and yellow stannic sulphide, SnS_2, from stannic salts.

$$SnCl_2 + H_2S = SnS + 2HCl$$
$$SnCl_4 + 2H_2S = SnS_2 + 4HCl$$

(2) With stannous salts, caustic soda produces a white precipitate of stannous hydroxide, $Sn(OH)_2$, soluble in excess of the reagent. With stannic salts it gives a white precipitate of $SnO(OH)_2$, also soluble in excess.

(3) Mercuric chloride with excess of stannous salts gives a white precipitate of mercurous chloride, HgCl, which gradually changes on boiling to a grey precipitate of mercury. Stannic salts do not react with mercuric chloride.

(4) Zinc precipitates, from solutions of stannous and stannic salts, metallic tin as a spongy mass.

(5) A stannic salt, boiled with hydrochloric acid and metallic copper, is reduced to the stannous condition. The solution will then reduce mercuric chloride.

(6) Solid tin compounds, heated on charcoal with potassium cyanide, are reduced to metallic tin. The beads formed are malleable, but will not mark paper. They are soluble in excess of dilute nitric acid. The solution on evaporation gives a white precipitate of metastannic acid.

CHAPTER XLIV

ARSENIC AND ITS COMMON COMPOUNDS

Exp. 215—To test for arsenic

Directions—

(1) To test for arsenic in the solid state mix a small quantity of the compound with powdered charcoal and sodium carbonate and heat the mixture in a small tube. A mirror of arsenic is obtained on the cool part of the tube.

(2) Pass sulphuretted hydrogen through a solution of an arsenic compound acidified with hydrochloric acid. Warm

and again pass the gas. Repeat until a yellow precipitate of arsenious sulphide, As_2S_3, is obtained. Sulphuretted hydrogen must be passed several times in order to reduce arseniates to arsenites, from which the arsenic is precipitated as sulphide.

(3) Heat some arsenic solution with nitric acid in order to oxidise the arsenic to arsenic acid ; add excess of ammonium molybdate solution, and warm for a short time. A yellow precipitate indicates the presence of arsenic.

(4) (Marsh's Test) Into a small flask, fitted with a thistle funnel and a delivery tube drawn out to a jet, put some arsenic-free zinc and dilute sulphuric acid. When the gas coming from the jet has been tested and found to be free from air, light the hydrogen at the jet. Down the funnel pour the arsenic solution, and hold a white glazed porcelain dish in the flame of burning hydrogen. A black stain of metallic arsenic, soluble in a solution of sodium hypochlorite, indicates the presence of arsenic.

Next, put out the flame, and pass the gas through a solution of silver nitrate. A black precipitate of metallic silver indicates the presence of arsenic.

Finally, warm the middle of the delivery tube with the bunsen flame. A mirror of arsenic should be formed near the heated portion.

ARSENIC, As=75

Arsenic is found to some extent in nature in the elementary state. It also occurs as sulphide, As_2S_2, in *realgar* or *ruby sulphur*, and as As_2S_3 in *orpiment*. The oxide is found in the flues of pyrites burners, owing to the presence of arsenic compounds in the pyrites.

The element can be obtained by heating in a hard glass tube a mixture of white arsenic and excess of powdered charcoal. A mirror of arsenic condenses on the cool parts of the tube.

$$As_4O_6 + 6C = 4As + 6CO$$

Properties—The crystals of resublimed arsenic are isomorphous with those of the elements phosphorus and antimony. These crystals are bright, steel-grey, and metallic-looking and they are permanent in air. They conduct electricity.

Arsenic can be obtained in three allotropic modifications by subliming the element rapidly in a stream of hydrogen. Near the heated portion of the tube it collects as crystals, further on as a black shining mass, and further still as a yellow powder. The black mass and the yellow powder are amorphous. The specific gravities of the three forms are—crystalline 5.7, black 4.7, and yellow 3.7. The black and the yellow are converted to crystalline arsenic by heating to 360° C.

The vapour is yellow, has a smell like that of garlic, and a density at 860° C. corresponding to a molecule As_4. At temperatures above 1700° C. the vapour density corresponds to a molecule As_2. In this, arsenic resembles phosphorus, which has four atoms in the molecule at moderate temperatures, and two atoms in the molecule at very high temperatures.

Heated in oxygen, arsenic burns with a bright white flame, forming arsenious oxide, As_4O_6. It is oxidised by nitric acid and sulphuric acid, and in a finely powdered state it burns spontaneously in chlorine, forming arsenic trichloride.

Arsenuretted hydrogen (*arsine*), AsH_3, is prepared by treating zinc arsenide with dilute sulphuric acid.

$$Zn_3As_2 + 3H_2SO_4 = 2AsH_3 + 3ZnSO_4$$

Mixed with much hydrogen it is obtained when a solution of arsenious oxide is put into a flask containing zinc and dilute sulphuric acid.

It is a colourless gas, very poisonous and offensive smelling. It burns with a lilac flame, forming arsenious oxide and water.

$$4AsH_3 + 6O_2 = As_4O_6 + 6H_2O$$

If it is passed through a heated tube, it is split into its elements and a mirror of arsenic is formed in the cool part of the tube. If the gas is passed through a solution of silver nitrate, silver is precipitated :—

$$6AgNO_3 + AsH_3 + 3H_2O = 6Ag + 6HNO_3 + H_3AsO_3$$

Arsenious oxide (*white arsenic*), As_4O_6, may be obtained by passing oxygen over arsenic heated in a tube. Some of the oxide collects on the cold part of the tube. The experiment must be carried out in a draught chamber, owing to the poisonous nature of the fumes. It is obtained as a secondary product in several metallurgical processes.

Properties—It is a white solid, which exists in three forms, viz., an amorphous form, a form crystallising in regular octahedral crystals, and a form crystallising in prismatic crystals.

The density of the vapour corresponds to the formula, As_4O_6.

The oxide is slightly soluble in water to a feebly acid solution, which may contain arsenious acid, H_3AsO_3. It is very poisonous. It is used in medicine in the treatment of some skin diseases.

Arsenites—Alkaline arsenites may be obtained by dissolving arsenious oxide in caustic alkalis. They are alkaline to litmus, and are decomposed by weak acids. All the arsenites, except those of the alkali metals, are insoluble. They are salts of the unstable acid, H_3AsO_3.

Arsenic oxide (*arsenic anhydride*), As_4O_{10}, is obtained by heating arsenic acid to dull redness.

$$4H_3AsO_4 = 6H_2O + As_4O_{10}$$

Arsenic oxide is a white deliquescent solid, which dissolves in water, forming arsenic acid. If strongly heated, it is decomposed to arsenious oxide and oxygen.

$$As_4O_{10} = As_4O_6 + 2O_2$$

Arsenic acid, H_3AsO_4, is obtained when arsenic or white arsenic is boiled for some time with strong nitric acid, and the solution is concentrated until crystals appear on cooling.

The crystals are known as ortho-arsenic acid, and they have the formula, $2H_3AsO_4.H_2O$. If the crystals are heated to 100° C., the anhydrous acid, H_3AsO_4, is obtained as a crystalline powder.

If the acid is heated to 180° C., pyro-arsenic acid, $H_4As_2O_7$, is formed.

$$2H_3AsO_4 = H_4As_2O_7 + H_2O$$

This, at 200° C., forms metarsenic acid, $HAsO_3$.

$$H_4As_2O_7 = 2HAsO_3 + H_2O$$

Heated to low redness, metarsenic acid gives the anhydride As_4O_{10}.

$$4HAsO_3 = As_4O_{10} + 2H_2O$$

Pyro-arsenic and *metarsenic acids* are crystalline solids, which dissolve in water, forming once again the ortho acid,

H_3AsO_4. They differ in this from pyro-phosphoric and metaphosphoric acids, which do not go back to the ortho acid immediately when dissolved.

Arsenic acid is tribasic, and the ortho-arsenates are isomorphous with the orthophosphates. The pyro-arsenates and metarsenates exist only in the solid state. They form ortho-arsenates when dissolved in water.

Arsenic chloride, $AsCl_3$, can be obtained by heating arsenic in a stream of chlorine, or by distilling a mixture of sodium chloride, arsenious oxide, and sulphuric acid.

$$As_4O_6 + 12HCl = 4AsCl_3 + 6H_2O$$

It is a colourless, fuming, oily liquid, very poisonous, and boiling at 130° C. With a small quantity of water it forms an oxychloride, $AsOCl.H_2O$, and with excess of water it forms arsenious oxide and hydrochloric acid. Thus :—

$$AsCl_3 + 2H_2O = AsOCl.H_2O + 2HCl$$
$$4AsCl_3 + 6H_2O = As_4O_6 + 12HCl$$

Arsenic disulphide, As_2S_2, is obtained as a red brittle powder when arsenious oxide and sulphur are heated together. It sublimes.

Arsenic trisulphide, As_2S_3, is obtained by heating sulphur and arsenic in the calculated quantities, or by passing sulphuretted hydrogen through a solution of arsenious oxide.

$$As_4O_6 + 6H_2S = 2As_2S_3 + 6H_2O$$

It is a yellow solid, which melts easily and sublimes unchanged. It burns in air, when heated, forming arsenious oxide and sulphur dioxide. It dissolves in alkalis or in alkaline sulphides with formation of thioarsenites, *e.g.*, K_3AsS_3. The thioarsenites are decomposed by acids to arsenic sulphide and sulphuretted hydrogen.

Arsenic pentasulphide, As_2S_5, is a yellow solid prepared by adding an acid to a solution of a thioarsenate.

$$2Na_3AsS_4 + 3H_2SO_4 = 3Na_2SO_4 + 3H_2S + As_2S_5$$

The sulphide is readily soluble in solutions of the sulphides of the alkali metals and ammonia with formation of thioarsenates, *e.g.*, K_3AsS_4. These are decomposed by acids as in the above equation.

Arsenic—a metalloid—A substance intermediate in char-

acter between metals and non-metals is sometimes called a *metalloid*. Arsenic has such a character. It has a metallic appearance and it conducts electricity well. It is a solid with a high vaporising point. It is opaque. It forms an unstable hydride. It alloys with metals. All these are metallic characters.

On the other hand, it exists in allotropic modifications, it is not malleable or ductile ; it forms acidic oxides ; and its chloride is decomposed by water. These are non-metallic characters. The formulæ of its compounds are almost perfectly analogous to those of the corresponding compounds of phosphorus. It is classed with phosphorus in the Periodic Classification.

CHAPTER XLV

SILVER AND ITS COMMON COMPOUNDS

Exp. 216—To test for silver

Directions—Carry out the following tests with solutions of silver salts, and try to write equations for the reactions :—

(1) Add dilute hydrochloric acid. Try to dissolve the precipitate in hot water, and then in ammonia.

(2) Add caustic soda solution.

(3) Add potassium iodide solution.

(4) Add potassium chromate solution.

(5) Heat a solid silver compound on charcoal with sodium carbonate. Note the hardness and solubility in acids of the metallic bead formed.

Exercises—Prepare specimens of the chloride, oxide, iodide and chromate from silver nitrate.

SILVER, Ag=108

Silver is found in nature in the free state, and alloyed with gold and other metals. It also occurs as *silver glance*, Ag_2S, as *horn silver*, AgCl, as *pyragyrite* or *ruby silver*, $3Ag_2S.Sb_2S_3$, and as other double sulphides. Much of the silver of commerce is obtained from argentiferous galena.

Extraction—

(1) **By Pattinson's process** (see lead).

(2) **By the Mexican amalgamation process.**

The ore is crushed, ground to a mud with water, spread on a circular floor, and mixed with about 5 per cent. of common salt by the treading of mules. After twenty-four hours, mercury together with *magistral* (a mixture of copper sulphate and ferric sulphate) is added and mixed by the treading of mules. More mercury is gradually added and mixed in, and after several days the amalgam is washed with running water, then strained through canvas bags to remove excess of mercury, and finally distilled.

It is probable that cuprous and cupric chlorides are formed by the action of the common salt on the copper sulphate. The copper chlorides then react with the silver sulphide of the ore forming silver chloride, and this is reduced to metallic silver by some of the mercury. Thus :—

$$Cu_2Cl_2 + Ag_2S = 2AgCl + Cu_2S$$
$$2CuCl_2 + Ag_2S = 2AgCl + Cu_2Cl_2 + S$$
$$2AgCl + 2Hg = 2Ag + Hg_2Cl_2$$

(3) **By other amalgamation processes.**

One such process consists in crushing the ore finely, placing it in revolving iron pans, and adding mercury when the ore has been reduced to a very fine state of division. The reaction is :—

$$Ag_2S + Hg = HgS + 2Ag$$

A second process consists in roasting the ore with common salt to convert the silver to chloride, mixing the finely crushed roasted ore with water, and putting the mixture into revolving barrels containing scrap iron. The reaction is :—

$$2AgCl + Fe = FeCl_2 + 2Ag$$

Properties—Silver is a bright, white metal, which is untarnished by pure air. It is rapidly tarnished by air containing sulphuretted hydrogen. Its specific gravity is 10.5. It melts at 950° C., and it can be distilled at very high temperatures. It is an excellent conductor of heat and electricity. Molten silver absorbs about 20 times its volume of oxygen, which it gives off on solidification.

Silver is not soluble in hydrochloric acid, but it dissolves readily in nitric acid with formation of silver nitrate and

oxides of nitrogen. It reacts with hot, strong sulphuric acid with formation of silver sulphate and sulphur dioxide.

Silver is hardened by alloying it with copper. English silver coins contain $7\frac{1}{2}$ per cent. of copper, and French silver coins contain 10 per cent. of copper. The copper deprives silver of its power of dissolving or occluding oxygen, so that castings made from the alloy are not spoiled by the evolution of oxygen on solidification.

Silver oxide (*argentic oxide*), Ag_2O, is obtained by adding caustic soda to a solution of silver nitrate. A brown hydrated oxide is precipitated, and from this the black amorphous oxide can be obtained by careful heating.

The oxide is slightly soluble in water, the solution having a metallic taste and an alkaline reaction.

It is a powerful oxidising agent. It gives off its oxygen if heated to about 300° C. It is a basic oxide.

A dioxide of silver, Ag_2O_2, is formed when a strong solution of silver nitrate is electrolysed. It is a basic peroxide, and it is a more powerful oxidising agent than the monoxide.

Silver chloride, $AgCl$, is prepared by adding a solution of a chloride to a solution of a silver salt. Silver chloride comes down as a white curdy precipitate. The precipitate is soluble in ammonia, or in potassium cyanide solution, with which it forms a double salt, AgCN.KCN. The double cyanide is used in silver-plating.

Silver chloride darkens when exposed to light, becoming first violet and finally almost black. The salt melts at 450° C., and sets on cooling to a horny mass, very like natural horn silver.

Silver nitrate (*lunar caustic*), $AgNO_3$, is prepared by dissolving silver in nitric acid. It crystallises in colourless tables, which melt easily and solidify again to a white mass, *lunar caustic*. When heated, silver nitrate first gives off oxygen and forms silver nitrite, and then splits into metallic silver and oxides of nitrogen. Silver nitrate blackens on exposure to light. Hence, it blackens the skin, and is used as a constituent of marking-ink. In the form of *lunar caustic* it is used as a caustic by doctors.

Silver sulphate, Ag_2SO_4, is a slightly soluble salt of silver, made by dissolving the metal oxide, or carbonate in sulphuric acid. With aluminium sulphate it forms an alum.

$$Ag_2SO_4.Al_2(SO_4)_3.24H_2O$$

Tests for silver—

(1) Dilute hydrochloric acid produces in silver solutions a white precipitate of silver chloride, soluble in ammonia but insoluble in hot water.

(2) Caustic soda produces a brown precipitate of the hydrated oxide.

(3) Potassium iodide precipitates yellow silver iodide, insoluble in ammonia.

(4) Potassium chromate produces a dark red precipitate of silver chromate, soluble in hot nitric acid.

(5) Heated on charcoal with sodium carbonate before the blow-pipe, silver salts are reduced to metallic silver.

Silver and copper—Silver, although in the same sub-group of the Periodic Classification, differs from copper very considerably. Silver is not oxidised by heating in air. Copper is. Silver forms only one series of salts. Copper forms cuprous and cupric salts. Silver salts are decomposed to the metal on strong heating. Copper salts are not. Silver chloride is very insoluble. Cuprous chloride is insoluble, but cupric chloride is soluble. The cuprous salts, which resemble the silver salts in some respects, are easily oxidised, whereas the silver salts cannot be oxidised.

In fact, a study of the compounds of silver would hardly cause one to classify it with copper.

CHAPTER XLVI

ELECTROLYSIS

You have already come across several cases of electrolysis. For example, acidulated water and strong hydrochloric acid solution were broken up into their elements when an electric current was passed through them. Such a decomposition by means of an electric current is called *electrolysis*. The liquid which conducts the current is called the *electrolyte*.

Electrolysis of copper sulphate solution—The electrolysis of copper sulphate solution is, chemically, fairly simple. When a current from several cells is passed between platinum electrodes through the solution, copper is deposited on the kathode or negative electrode, oxygen comes off at the anode

or positive electrode, and sulphuric acid gradually accumulates in the liquid.

The direction of the current in the wire and through the electrolyte is shown in Fig. 127. **K** = kathode ; **A** = anode.

It is generally believed that when copper sulphate, or any other substance which forms a conducting solution, is dissolved in water, many of the molecules of the dissolved substance are split up into simpler particles which are called *ions*. These ions carry considerable charges of electricity. Hydrogen and the metals form positive ions carrying positive electricity ; acid radicles and the group OH form negative ions carrying negative electricity. When a current of electricity is passed through a liquid containing such ions, the current is actually carried through the electrolyte by the ions. The current does not produce the ions ; it only directs them. The positive ions give up their charge to the negative electrode, and the negative ions to the positive electrode. Their charges once given up, the ions assume the ordinary properties of the element or group of elements of which they are composed, and are deposited on the electrodes. They then come off as gases, or remain as a solid deposit on the electrode, or react with the electrode or with the solvent. In the case of copper sulphate the ions are Cu and SO_4. The Cu ion, which is charged positively, is deposited on the kathode as metallic copper, after it has given up its charge to the kathode. The SO_4 ion, charged negatively, gives up its charge to the anode. It can then no longer exist as SO_4. It reacts at once with water, giving sulphuric acid and oxygen.

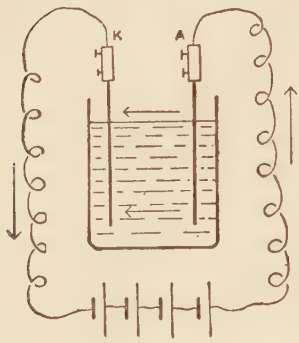

FIG. 127

$$2SO_4 + 2H_2O = 2H_2SO_4 + O_2$$

The sulphuric acid collects in the liquid round the anode, and the oxygen is given off from the anode.

If a copper anode is used the products are different. The copper of the anode combines with the SO_4 set free, forming

copper sulphate, which replaces the copper sulphate decomposed by the current. The effect of the passage of the current is therefore a transference of copper from anode to kathode. Similarly, when a solution of zinc sulphate is electrolysed between a zinc anode and a platinum or zinc kathode, as much zinc is dissolved from the anode as is deposited on the kathode.

Electrolysis of acidulated water with platinum electrodes—Water is not an electrolyte, that is, it is not dissociated into ions, and consequently it does not conduct an electric current. When a few drops of sulphuric acid are dissolved in the water, the ions H and SO_4 are at once formed. The positive ion, or kation, H, gives up its charge to the kathode and comes off as hydrogen; the negative ion, or anion, SO_4, gives up its charge to the anode and then reacts with water, forming sulphuric acid and oxygen. The oxygen comes off at the anode. The changes may be expressed by the equations:—

$$H_2SO_4 = 2H + SO_4$$
$$SO_4 + H_2O = H_2SO_4 + O$$

It is obvious, from the equations, that as much sulphuric acid is formed as is decomposed, and that the final result is the splitting of water into hydrogen and oxygen.

Electrolysis of sodium chloride solution—Here the ions are Na and Cl. As soon as the kation, Na, has given up its positive charge to the kathode, it assumes the ordinary properties of sodium and decomposes water, forming caustic soda and hydrogen. The hydrogen is given off from the kathode, and caustic soda is formed in the liquid near the kathode. The anion, Cl, gives up its negative charge to the anode and assumes the ordinary properties of chlorine. Some of the chlorine attacks the platinum electrode and forms platinic chloride, some escapes, some dissolves in the water, and, if the solution is very dilute, some decomposes water, forming hydrochloric acid and setting free oxygen.

Products, such as the caustic soda and oxygen, are called *secondary products* of electrolysis.

First Law of Faraday—Faraday, in 1833, by a series of careful experiments, established the law that the *amounts of substances deposited at the electrodes are strictly proportional to the quantity of electricity passed through the electrolyte.* This

means that a current of two amperes,* passed through copper sulphate solution for ten minutes, will cause the deposition of twice as much copper as a current of one ampere passed for the same time.

It is obvious, therefore, that equal weights of copper carry equal amounts of positive electricity, *i.e.* the Cu ions, if of the same size, must carry equal charges. What is true for copper is true for other substances.

Second Law of Faraday—When the same current is passed through several electrolytes, the amounts of the substances deposited on or set free at the electrodes are proportional to the chemical equivalents of the substances. Thus, if a current is passed through copper sulphate solution, acidified water, silver nitrate solution, hydrochloric acid, the weights of copper, hydrogen, oxygen, silver, and chlorine set free in the different cells are in the proportion 31.5 of copper to 1 of hydrogen, to 8 of oxygen, to 108 of silver, to 35.5 of chlorine. These numbers are the chemical equivalents of the substances.

The second law may be stated: *the liberation of chemically equivalent amounts of the products of electrolysis is caused by the passage of equal quantities of electricity through electrolytes.*

The weight of a substance liberated by the passage of one coulomb† of electricity is called the *electro-chemical equivalent* of the substance. The electro-chemical equivalent of hydrogen is 0.00001038 gram. The electro-chemical equivalent of other elements can be obtained by multiplying the electro-chemical equivalent of hydrogen by the chemical equivalent of the element. Thus, the electro-chemical equivalent of copper is $0.00001038 \times 31.5 = .000327$.

Electrolytic dissociation—You have seen that certain salts and acids, when dissolved in water, are to some extent dissociated into ions. All chemical substances are not so dissociated in solution. For example, solutions of sugar, gum, alcohol, and many other organic substances do not conduct a current of electricity, *i.e.* these substances are not dissociated into ions. Solutions of salts, alkalis, and mineral acids, on the other hand, are good electrolytes. The great majority of the molecules of such substances are dissociated

* An *ampere* is the practical unit of current.

† The *coulomb* is the quantity of electricity carried in one second past any point of a circuit through which a current of one ampere is flowing.

into ions when the compounds are dissolved in water; the greater the dilution, the greater the dissociation until, when the solution is about one thousandth normal, $\frac{N}{1000}$, dissociation into ions is practically complete. If, therefore, you were to find the molecular weights of these substances by lowering of freezing-point (see p. 107), or raising of the boiling-point of the solution, you ought to get a value much less than the true molecular weight of the substance, just as you find too low a value for the molecular weight from the density of substances which dissociate when vaporised. Such is the case. A dilute solution of common salt, for example, gives for the molecular weight a value which is only slightly more than half that corresponding to the formula NaCl. This indicates that sodium chloride is almost completely dissociated into Na ions and Cl ions.

A solution of an electrolyte contains equal numbers of positive and negative ionic charges, and is therefore electrically neutral. A positive ion carrying one positive charge is represented by the symbol of the element or group with one dot placed above it. Thus, $H^{\cdot}$ represents a hydrogen ion, and $NH_4^{\cdot}$ an ammonium ion. The divalent and trivalent elements have ions carrying two or three positive charges and are represented thus: zinc ion $Zn^{\cdot\cdot}$, ferric ion $Fe^{\cdot\cdot\cdot}$. In a similar way the charges carried by negative ions are represented by dashes. Thus, Cl' is a chlorine ion, OH' a hydroxyl ion, and SO_4'' a sulphate ion. A solution of zinc chloride would therefore contain zinc ions $Zn^{\cdot\cdot}$ and twice as many chlorine ions Cl'. If the solution were not very dilute there would be present a considerable percentage of un-ionised zinc chloride $ZnCl_2$.

An acid has been defined as a substance which, when dissolved in water, produces hydrogen ions. A "strong" acid, therefore, should be regarded as an acid which is largely ionised in solution. Similarly, a "strong" base is largely ionised in solution. Hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) are largely ionised in solution and are strong acids; caustic soda (NaOH) and caustic potash (KOH) are largely ionised and are strong bases. Oxalic acid ($H_2C_2O_4$) and hydrocyanic acid (HCN) are weak acids and are only slightly ionised; ammonium hydrogen (NH_4OH) and ferric

hydroxide $Fe(OH)_3$ are weak bases and are only slightly ionised. Solutions of bases are basic on account of the presence of OH ions.

If a strong acid and a strong base in solution are brought together the H ions of the acid combine with the OH ions of the base to form un-ionised water, and a salt is formed. All soluble salts are strongly ionised and therefore the positive ions of the acid and the negative ions of the base still remain in the ionised state. Thus, when dilute hydrochloric acid solution is added to a dilute solution of caustic soda the reaction may be represented—

$$H^{\cdot} + Cl' + Na^{\cdot} + OH' = HOH + Na^{\cdot} + Cl'$$

If, however, the salt formed is insoluble it is not ionised. Thus, if sulphuric acid solution is added to barium hydroxide solution the reaction may be represented—

$$H2^{\cdot} + SO_4'' + Ba^{\cdot\cdot} + 2OH' = 2HOH + BaSO_4$$

No ions are left in the solution.

Water is itself ionised to the extent of about one in ten million into $H^{\cdot}$ and OH' ions. The consideration of the effect of this ionisation is, however, beyond the range of this book.

Application of electrolytic dissociation to analysis of salts—The dissociation of salts dissolved in water into their ions is utilised in testing for metals and acids in qualitative analysis. About 24 common metals and about as many acids are usually tested for. The possible salts these metals and acids can form are over 500 in number. If special tests were necessary for each of these 500 salts, analysis would become almost impossible. Actually, only the ions, about 48 in number, are tested for. For example, no matter whether copper be combined with Cl, SO_4, NO_3, $CH_3.COO$, etc., a copper ion is present when the salt is dissolved. A reagent, which will produce an insoluble and, therefore, un-ionised substance is added. In the case of copper salts, sulphuretted hydrogen, or caustic soda, which would produce insoluble precipitates of copper sulphide or copper hydroxide, would be good reagents. Whatever the acid radicle may be, with a few rare exceptions, the same insoluble precipitate is produced by the combination of the metallic ion with one of the ions of the reagent. Any barium salt solution will give a white precipitate of barium sulphate when dilute sulphuric acid is added, or any chloride solution will give a white precipitate

of silver chloride when nitric acid and silver nitrate are added. Thus—

$$Ba^{\cdot\cdot} + 2Cl' + 2H^{\cdot} + SO_4'' = BaSO_4 + 2H^{\cdot} + 2Cl'$$
$$Ag^{\cdot} + NO_3' + Na^{\cdot} + Cl' = AgCl + H^{\cdot} + NO_3'$$

Practical application of electrolysis

Electro-plating—The object to be plated is thoroughly cleansed, and its surface is slightly roughened. It is then placed as kathode in a solution of a suitable salt of the metal to be deposited, with a plate of the metal itself as anode. An electric current is passed until a sufficiently thick film of the metal has been deposited on the object.

When an object is to be coated with copper, a bath of copper sulphate solution may be used. If the object is made of iron, copper sulphate is unsuitable for the bath, as iron causes the deposition of copper without the passage of a current. This chemically deposited copper does not adhere to the iron sufficiently well. The copper sulphate bath is therefore replaced by a bath of copper sodium tartrate, obtained by adding excess of caustic soda to a solution of a mixture of copper sulphate and tartaric acid.

Silver is deposited from a bath of the soluble double cyanide of silver and potassium $KAg(CN)_2$. Excess of potassium cyanide is used in order to prevent the deposition of silver cyanide on the silver anode.

Gold is deposited from a bath of the double cyanide of gold and potassium, $KAu(CN)_2$.

Nickel is deposited from a bath of a slightly acid solution of nickel ammonium sulphate, $NiSO_4.(NH_4)_2SO_4.6H_2O$, saturated at a temperature of 20° to 25° C. The best nickel plate is made by electro-coppering the object, and then depositing the nickel on the film of copper.

Electro-typing—By this process statues, busts, and similar works of art can be reproduced in copper, and wood-cuts can be copied. Models of statues, busts, etc., are made in gypsum or gutta-percha. They are then saturated with oil, and coated with graphite to make the surface a conductor. The object is made the kathode in a bath of copper sulphate solution, and a current is passed until a coating of copper, one-sixteenth of an inch thick, is formed. The copper is cut into several pieces and the plaster core removed. The inner surface of these pieces is then coated with copper sulphide by treating

with sulphuretted hydrogen. The pieces are again put into the bath until a sufficiently thick layer of copper is deposited on the inner surface. The copper sulphide separates the deposit from the original copper, which is now stripped off. The inner portions, which are exact reproductions of parts of the model, are joined together.

Wood-cuts are copied by taking a reverse of the wood-cut in softening gutta-percha, covering the reverse with graphite powder, and using it as the kathode in a copper sulphate bath, until a sufficiently thick film of copper is deposited. The copper is then removed from the cast, and the back of the copper cast is filled with type metal or fusible solder. In this way wood-cuts can be copied with great accuracy.

Electrolytic manufacturing processes—Aluminium is now prepared by electrolysis of fused aluminium oxide, or of aluminium oxide dissolved in fused cryolite, Na_3AlF_6. Sodium is manufactured by electrolysis of fused caustic soda. Caustic soda, hypochlorites, and chlorates can be made on the large scale by electrolysis of sodium chloride solution.

Copper may be refined electrolytically by making the impure copper the anode in an acid bath of copper sulphate solution. Pure copper is deposited on a thin sheet of copper acting as kathode. Impurities of arsenic, antimony, and iron go into solution, and a sludge containing silver and gold is deposited.

CHAPTER XLVII

THE PERIODIC CLASSIFICATION

In 1815 and 1816 there appeared two anonymous papers dealing with the atomic weights of the elements and with the specific gravity of their vapours. In these papers it was suggested that the atomic weights of the elements (fourteen elements given) were exact multiples of the atomic weight of hydrogen. Afterwards Prout, known then as the author, published his hypothesis that *hydrogen was a primary matter of which all the other elements were formed by various condensations.*

Prout's hypothesis was welcomed by some chemists, but criticised adversely by others, including Berzelius. It was

revived by Dumas and Stas in 1841, but the atomic weight of chlorine (35.5) was an obstacle, and the atomic weights of several other elements, *e.g.*, copper and lead, could not be regarded by conscientious chemists as whole numbers. Marignac suggested that half the atomic weight of hydrogen might be taken as the unit of atomic weight. Dumas supported this suggestion, but as facts accumulated he was compelled to take a quarter of the atomic weight of hydrogen as unit. The accurate atomic weight determinations of Stas and others soon showed, however, that Prout's hypothesis was untenable.

About 1816 Döbereiner and later (1851) Dumas pointed out that many chemically similar elements fell into groups of three (triads), and that the atomic weights of such elements were either almost the same, or showed a constant difference. An example of the former group of triads is, iron 55.84, cobalt 58.97, and nickel 58.68; and an example of the latter, chlorine 35.46, bromine 79.92, and iodine 126.92. It was thought that all the elements might in time be grouped into triads, but later it was shown by Cooke that the grouping into triads broke up such natural groupings as those of the four halogens and the alkali metals.

Various classifications founded on chemical properties were also suggested, but it was not until Newlands, in 1864, brought forward his Law of Octaves that a natural classification was produced. According to this law when the elements are arranged in the order of their atomic weights, they fall naturally into rows of seven, the eighth element possessing similar properties to those of the first, the fifteenth similar properties to those of the first and eighth, and so on. The classification was very imperfect owing to the comparatively small number of elements known, and to the lack of accuracy in many atomic weight determinations. His table is shown below.

H	F	Cl	Co, Ni	Br	Pd	I	Pt
Li	Na	K	Cu	Rb	Ag	Cs	Os
Be	Mg	Ca	Zn	Sr	Cd	Ba	Hg
B	Al	Cr	Y	Ce	U	Ta	Tl
C	Si	Ti	In	Zr	Sn	W	Pb
N	P	Mn	As	Di	Sb	Nb	Bi
O	S	Fe	Se	Rh, Ru	Te	Au	Th

Newlands' classification received very little attention from chemists and seems to have been forgotten. In 1869 the Russian chemist Mendelejeff and the German chemist Lothar Meyer, each independently of one another, and in ignorance of Newlands' work, published the classifications which are known to-day as the Periodic Classification. Mendelejeff's table differs from the modern table shown on page 429 only in the omission of the group O of inert elements and of other elements then unknown. Mendelejeff stated his Periodic Law as follows :—

The elements, if arranged according to their atomic weights, exhibit an evident periodicity of properties.

Examination of the table shows first that hydrogen stands alone. In the table on page 429 it is placed at the head of Group I, but, as we shall see later, it might equally well be placed at the head of Group VII. Possibly, it should be omitted entirely from the table.

Next come two so-called "short periods," each consisting of eight elements, the first, second, etc., elements of the first period, resembling closely the first, second, etc., elements of the second period.

The first "long period" consists of eighteen elements all of which are known. It will be noticed that in this and the subsequent long periods it is the alternate elements in the vertical columns which resemble each other closely. Thus, in Group I potassium, rubidium, and cæsium are very much alike, but differ considerably in properties from copper, silver, and gold ; and in Group II calcium, strontium, and barium are very similar, but differ somewhat from magnesium, zinc, and cadmium. The long period arrangements brings the elements of Group VIII. into a graduated series of elements, which show an orderly change in properties from the alkali metals, potassium and rubidium, to the non-metals, bromine and iodine.

The third and fourth long periods are incomplete and the fifth long period can hardly be called long as it contains only six known elements.

More detailed examination of the table brings out many interesting facts. As we pass from left to right along the horizontal rows we notice in the short periods a gradual change from strong metallic character in Group I to equally

Atomic weights in ordinary type.] THE PERIODIC TABLE [Atomic numbers in black type

	Group O	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
First short period		H 1.008 1							
	He 4.00 2	Li 6.94 3	Be 9.1 4	B 10.9 5	C 12.0 6	N 14.01 7	O 16.0 8	F 19.0 9	
Second short period	Ne 20.2 10	Na 23.0 11	Mg 24.32 12	Al 26.96 13	Si 28.3 14	P 31.04 15	S 32.06 16	Cl 35.45 17	
First long period	A 39.9 18	K 39.1 19	Ca 40.07 20	Sc 45.1 21	Ti 48.1 22	V 51.06 23	Cr 52.0 24	Mn 54.93 25	Fe 55.84 26 / Co 58.97 27 / Ni 58.68 28
		Cu 63.57 29	Zn 65.37 30	Ga 70.1 31	Ge 72.5 32	As 74.96 33	Se 79.2 34	Br 79.92 35	
Second long period	Kr 82.92 36	Rb 85.45 37	Sr 87.83 38	Y 89.33 39	Zr 90.6 40	Nb 93.5 41	Mo 96.0 42	— 43	Ru 101.7 44 / Rh 102.9 45 / Pd 106.7 46
		Ag 107.88 47	Cd 112.4 48	In 114.8 49	Sn 118.7 50	Sb 120.2 51	Te 127.5 52	I 126.92 53	
Third long period	X 130.2 54	Cs 132.81 55	Ba 137.37 56	La 139.0 57	Ce 140.25 58	—	—	—	— — —
		—	—	—	—	—	—	—	
Fourth long period		—	—	—	—	Ta 181.5 73	W 184.0 74	— 75	Os 190.9 76 / Ir 193.1 77 / Pt 195.2 78
		Au 197.2 79	Hg 200.6 80	Tl 204.0 81	Pb 207.2 82	Bi 209.0 83	Po 84	— 85	
Fifth long (?) period	Nt 222.0 86	— 87	Ra 226.0 88	Ac 89	Th 232.15 90	UXii 91	U 238.2 92		
Formulæ of oxides	—	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4
Formulæ of hydroxides	—	RH	RH_2	RH_3	RH_4	RH_3	RH_2	RH	—

NOTE.—The elements of atomic numbers 59 to 72 have been omitted from the table as their properties are not sufficiently characteristic for definite places to be assigned to them. Atomic numbers 43, 61, 75, 85 and 87, belong to undiscovered elements.

strong non-metallic character in Group VII. In the long periods there is the same change, but it is more gradual, and the metallic character is maintained through the eighth group elements, and more than half way through the second half of the period, *e.g.*, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, *As*, *Se*, *Br*. The symbols of the non-metallic elements are printed in italics.

The elements of Group O form a neutral territory between the electro-negative (non-metallic) halogens of Group VII and the electro-positive (metallic) alkali metals of Group I.

Again, as we pass from top to bottom of a group we notice an increase of metallic character, *e.g.*, carbon to lead in Group IV, and nitrogen to bismuth in Group V.

The valency of the elements towards hydrogen increases from one in Group I to four in Group IV, afterwards dropping regularly to one in Group VII. The valency in oxygen compounds on the other hand increases from one in Group I to eight in Group VIII. There are exceptions to this. For example, copper has a valency of two in cupric oxide, and gold a valency of three in auric oxide. Calcium and barium form peroxides CaO_2 and BaO_2 in which the valency may be four.

The specific gravity of the elements increases to a maximum at the centre of each period, and is at its lowest at the ends. Thus, in the second short period and in the first long period the specific gravities are—

						Na	Mg	Al	Si	P	S	Cl				
						.97	1.74	2.56	2.5	2.0	1.9	1.4				
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
.87	1.6	3.8	4.87	5.5	6.8	7.4	7.9	8.7	8.8	8.8	7.0	5.9	5.5	5.7	4.4	3.1

The periodicity of this property is strikingly brought out in Lothar Meyer's Atomic Volume curve. The atomic volume is the volume occupied by the atomic weight of an element, and is obtained by dividing the atomic weight by the specific gravity.

It will be noticed that each apex is occupied by an alkali metal, and that elements with similar chemical properties are found at similar parts of the curve. Thus, on the ascending portions are found the halogens fluorine, chlorine, bromine, and iodine; on the descending portions the alkaline earths calcium, strontium, and barium; and near the base the elements in the middle of the period, long or short.

A similar curve can be obtained with the melting-points of the elements, absolute temperatures being used. In this

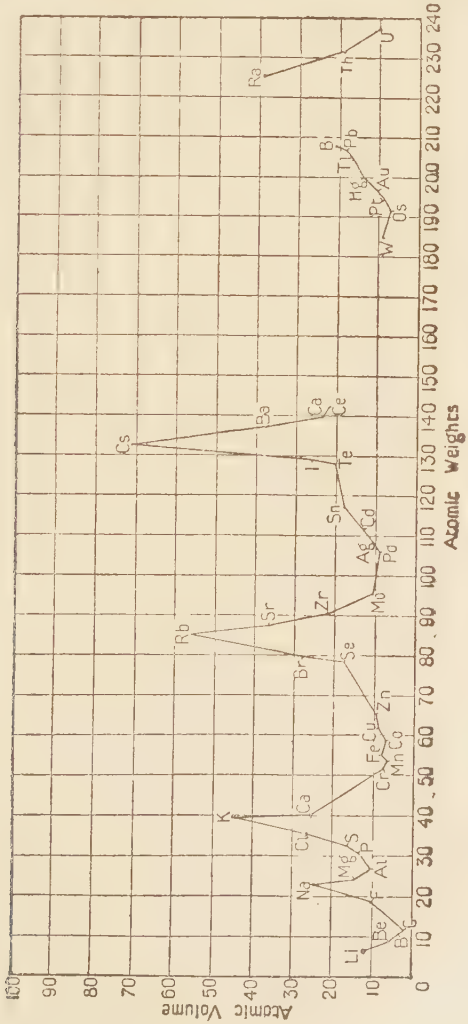
Atomic Volume
Atomic Weights
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240
10 20 30 40 50 60 70 80 90 100
Li Be B C Na Mg Al Si P S Cl K Ca Cr Mn Co Fe Cu Zn Br Se Rb Sr Zr Mo Ag Cd Sn Te I Cs Ba Ce Ta W Os Ir Pt Au Hg Tl Pb Bi Ra Th U

FIG. 128

case, however, the positions of the elements are approximately reversed, the alkali metals and the halogens having the lowest melting-points and the elements of the middle of the periods the highest melting-points.

Other physical properties with the exception of atomic heat show similar variations, but the regularities are not as sharp and definite as could be desired.

It would appear from a consideration of these physical properties and of the chemical properties that an arrangement of the elements, such as that shown below, might bring out more clearly the relations between the elements.

(1)	He	Li											Be	B	C	N	O	F
(2)	Ne	Na											Mg	Al	Si	P	S	Cl
(3)	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
(4)	Kr	Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
(5)	X	Cs	Ba	La	Ce (etc.)	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—
(6)	Nt	—	Ra	Ac	Th	Uxii	U											

This table omits all the elements of indeterminate character between cerium and tantalum, shows closely allied elements in the vertical groups, and gets rid of such anomalies as the placing in Group VII manganese and chlorine, and in Group I the alkali metals and copper, silver and gold.

Position of hydrogen—The position of hydrogen has already been referred to. Its valency points to a position in the first or seventh group. Its low boiling-point, its non-metallic physical properties, and its di-atomic molecules show similarity to the corresponding properties of the halogens. Further, hydrogen forms hydrides which do not conduct electricity, and which, therefore, do not resemble the alloys of the metals; and hydrogen also replaces and is replaced by halogens in organic compounds.

On the other hand the most stable compounds of hydrogen are those which it forms with the non-metals, and the compounds of hydrogen with the halogens are stable and unlike the unstable compounds which the halogens form among themselves. Further, hydrogen in acids is readily replaced by metals. It would seem that hydrogen cannot satisfactorily be classed either with the alkali metals nor with the halogens. Hydrogen appears to stand alone and might very well be omitted from the classification.

Applications of the Periodic Classification—

When Mendelejeff made his table there were in it three gaps now occupied by gallium, germanium, and scandium. He predicted the existence of these elements and he stated their properties. Gallium was discovered by Lecocq de Boisbaudron in 1875, scandium by Nilson in 1879, and germanium by Winkler in 1887. The properties of these elements and of their compounds were found to correspond closely to those predicted by Mendelejeff, who based his predictions on the properties of neighbouring elements in the table. Below is shown a comparison of the properties of Mendelejeff's "ekasilicon" and the actual properties of germanium.

Ekasilicon	*Germanium*
Atomic weight, 72.	Atomic weight, 71.8.
Specific gravity, 5.5.	Specific gravity, 5.47.
Oxide EsO_2 of specific gravity, 4.7.	Oxide GeO_2 of specific gravity, 4.7.
Chloride, $EsCl_4$, a liquid boiling slightly below 100° C., and of specific gravity 1.9.	Chloride, $GeCl_4$, a liquid boiling at 86° C., and of specific gravity 1.887.
Ethide, $Es(C_2H_5)_4$, a liquid boiling at 160° C., and of specific gravity 0.96.	Ethide, $Ge(C_2H_5)_4$, a liquid boiling at 160° C., and of specific gravity slightly less than that of water.
Fluoride, EsF_4, not gaseous.	Fluoride, $GeF_4.3H_2O$, a white solid mass.

It will be seen that Mendelejeff's predictions were strikingly accurate.

The periodic classification also led to the revision of the atomic weights of beryllium, indium, uranium, and cæsium, since the atomic weights of these elements brought them into false positions in the table. Redeterminations established the present atomic weights and the elements then fell naturally into the positions they now occupy.

In the table it will be seen that tellurium has an atomic weight 127.5, which is greater than that of iodine (126.92), which follows it. Tellurium has properties which place it with certainty in the sulphur family. Much research has failed to bring down the atomic weight of tellurium to a value less than that of iodine. The position of tellurium appears, therefore, to be anomalous. Similarly, argon (39.9)

has a greater atomic weight than potassium (39.1), which follows it.

Both these anomalies have been explained since the discovery that *atomic number* rather than *atomic weight* is the fundamental characteristic of an element, and that many elements can exist in two or more forms, *isotopes*, of differing atomic weight.

The consideration of atomic numbers, isotopes, and the structure of the atom is beyond the scope of this book. Suffice it to say that the atoms are now regarded as composed of heavy nuclei, consisting of hydrogen atoms (*protons* positively charged) bound together by negative electrons. Rotating round this nucleus are negative electrons. The atom as a whole is neutral, the number of free positive charges on the nucleus being equal to the number of rotating electrons. The atom may be compared to a small solar system, the nucleus being the sun, and the negative electrons, rotating round the nucleus at comparatively great distances, being the planets. The number of planetary bodies or negative electrons fixes the *atomic number* of the element.

Some conception of the meaning of an *isotope* may be obtained by consideration of chlorine. The atomic weight of chlorine is approximately 35.5, taking the atomic weight of oxygen as 16. Obviously if all atoms are built of hydrogen atoms it must be a mixture of atoms of different weight. Aston has shown by means of X-ray spectra that it consists of a mixture of atoms of weights 35 and 37. These atoms, although differing in weight, have the same atomic number (17), and therefore the same chemical properties. They are known as *isotopes*. The nucleus of the atom weighing 35 would consist of 35 protons and 18 electrons, thus leaving a positive charge of 17 on the nucleus. The atom is rendered neutral by the rotation of 17 electrons round the nucleus.

The nucleus of the second isotope of chlorine, weighing 37, would consist of 37 protons and 20 electrons, thus again leaving a positive charge of 17 on the nucleus. The atom is again rendered neutral by the rotation of 17 electrons round the nucleus.

In the periodic classification figured on page 429, the atomic numbers are shown in black type.

APPENDIX I

ANALYSIS OF A SIMPLE SALT

In the tables given in the following pages the metals and acids are divided into small groups by taking advantage of the insolubility of various compounds of the metals and acid radicles. In the examination of a solution for the presence of a metal, it is all-important that the tests should be carried out in the order of the groups. Group I must be tested for before Group II, Group II before Group III, and so on. Neglect of this order of testing will cause confusion. Thus, if a solution contained lead, the reagents for Group IV would give a black precipitate, those for Group V would give a white precipitate, those for Group III will give a white precipitate. Consequently, lead might be thought to be cobalt or nickel, barium, strontium or calcium, or aluminium, according to the group reagent added. If, however, the testing is carried out in the proper manner, a white precipitate is obtained in Group I, and the tests given for the purpose of distinguishing the metals of this group readily show that the metal present is lead.

The group test is placed at the head of each table. If this test yields no precipitate, the tests for distinguishing the metals of that group need not be carried out. The group test for the following group should be proceeded with, and so on until the metal is proved to belong to a particular group.

The student should not use the tables mechanically. He should try to understand the object of each test. If he does his work intelligently, he will learn much about the preparation and properties of many salts of the metals.

The contractions used in the tables are—

O.S. = original solution.
ppt. = precipitate.
The chemical symbols for names of elements.
The chemical formulae for names of compounds.

PRELIMINARY ANALYSIS OF SIMPLE SALT FOR BASE

Experiment	Observation	Inference
1. Heat the solid in a dry tube	Alkaline water given off	NH_4 salt
	Yellow sublimate or red globules	Sulphides or sulphur
	White sublimate	Salt of NH_4, Hg, Sb, or As
	Metallic mirror	Hg or As

PRELIMINARY ANALYSIS OF SIMPLE SALT FOR BASE—*Ctd.*

Experiment	Observation		Inference
2. If a sublimate is obtained in (1), heat the solid in a tube with solid Na_2CO_3 and powdered charcoal	Black mirror which becomes white when heated in a tube open at both ends		As
	Grey sublimate or mirror which gives globules when rubbed with a rod		Hg
	Smell of ammonia		NH_4
3. Heat on charcoal before the blow-pipe	Residue is yellow while hot, white when cold		Zn
	Volatilises		NH_4, Hg, As, or Sb
	Burns away		S, C, etc.
	Green mass formed		Cr
	Deflagrates		Nitrate, chlorate etc.
4. Treat the white residue from (3) with a drop of $Co(NO_3)_2$ solution, and heat again	Blue mass		Al, or phosphate
	Bright green mass		Zn
	Dirty bluish-green mass		Sn
	Pale pink mass		Mg
5. Mix with solid Na_2CO_3 and solid KCN, and heat on charcoal before the blow-pipe	Red malleable metallic scales		Cu
	Malleable bead with yellow incrustation*		Pb
	Malleable bead without incrustation		Ag
	Malleable bead ; slight incrustation, yellow while hot		Sn
	Brittle bead ; orange or yellow incrustation		Bi
	Brittle bead; white incrustation		Sb
	Brown incrustation		Cd
	Smell of garlic		As
	Smell of ammonia		NH_4
6. Heat a small quantity of borax in a loop of platinum wire until a clear bead is obtained. Dip this bead into a small quantity of the substance and heat again	*Reducing flame*	*Oxidising flame*	
	Green	Green	Cr
	Bottle green	Reddish yellow hot ; pale yellow cold	Fe
	Red	Green hot; blue cold	Cu
	Colourless	Amethyst (violet)	Mn
	Blue	Blue	Co
	Grey	Brownish-violet	Ni

* The " incrustation " is formed, not on the bead, but on the charcoal surrounding the place where the substance has been heated.

PRELIMINARY ANALYSIS OF SIMPLE SALT FOR BASE—*Ctd.*

Experiment	Observation	Inference
7. Heat the substance moistened with strong HCl on a clean platinum wire in the edge of the bunsen flame	Red coloration lasting a long time	Ca
	Crimson coloration lasting a long time	Sr
	Pale green coloration lasting a long time	Ba
	Bluish-green coloration lasting a short time	Cu
	Violet coloration	K
	Intense yellow coloration	Na
	Bluish coloration	As, Pb, Sb, etc.

EXAMINATION FOR THE METAL IN A SIMPLE SALT

Take enough solid to cover a sixpence. Try to make a solution in water. If the salt is insoluble, try to get a solution in either (1) Dilute HCl, (2) Dilute HNO_3, (3) Strong HNO_3, (4) Aqua regia. Aqua regia consists of a mixture of three parts of strong HCl with one part of strong HNO_3.

If a solution in strong acid is obtained, most of the acid must be driven off, and the remaining solution largely diluted before the metals are tested for.

If the solid is not dissolved by any of the above solvents, fuse it with at least 5 times its weight of solid sodium carbonate, and extract the fused mass first with hot water and then with hot dilute HCl. Filter from insoluble solid, and test both solutions for the metals.

Test portions of your solution as follows :—

Group I.—Add dilute HCl. A white precipitate of an insoluble chloride indicates the presence of a *lead*, *silver*, or *mercurous* salt. Pour off the liquid from ppt., and shake ppt. with excess of NH_4OH.

Experiment	Silver	Mercurous	Lead
HCl ppt. shaken with NH_4OH	Ppt. dissolved	Ppt. blackened owing to formation of $NH_2.Hg_2Cl$	Ppt. undissolved
To O.S. add KI solution	Pale yellow ppt. of AgI, insoluble in boiling water	Dark green ppt. of HgI	Bright yellow ppt. of PbI_2, soluble in boiling water
Heat on charcoal with Na_2CO_3	Malleable bead which does not mark paper	Volatilises	Malleable bead which marks paper

Group II.—Add dilute HCl, and pass H_2S for a minute. Warm the solution, and again pass H_2S. Dilute with water and filter. Wash ppt. with water. Remove ppt. to a test-tube, and warm it with $(NH_4)_2S$ for a short time.

If ppt. is *soluble* in $(NH_4)_2S$, pass on to the sub-group.

If ppt. is *insoluble* in $(NH_4)_2S$, test as follows :—

Experiment	Lead	Mercuric	Bismuth	Copper	Cadmium
H_2S ppt. is	Black PbS	Black HgS	Black Bi_2S_3	Black CuS	Yellow CdS
To O.S. add NaOH solution	White ppt. of $2PbO.H_2O$, soluble in excess	Yellow ppt. of HgO, insoluble in excess	White ppt. of $Bi(OH)_3$ goes yellow on boiling	Pale blue ppt. of $Cu(OH)_2$; boiled with excess of NaOH goes black	White ppt of $Cd(OH)_2$ insoluble in excess
Heat on charcoal with KCN	Malleable bead; marks paper	Volatilises	Brittle bead; yellow crust	Red scales of metallic copper	Brown crust of CdO

Group II. (*Sub-group*)—H_2S ppt. is soluble in $(NH_4)_2S$.

Experiment	Tin (Stannous)	Tin (Stannic)	Antimony	Arsenic
H_2S ppt. is	Dark brown SnS	Yellow SnS_2, insoluble in $(NH_4)_2CO_3$ solution	Orange Sb_2S_3	Yellow As_2S_3 soluble in $(NH_4)_2CO_3$ solution
To O.S. add a few drops of $HgCl_2$ solution	White ppt., turning grey on boiling	No ppt.	———	———
Marsh's test (see explanation of tables)	———	———	Stain insoluble in sodium hypochlorite solution	Stain soluble in sodium hypochlorite solution
Heat on charcoal with KCN	Malleable metallic bead; does not mark paper	Malleable metallic bead; does not mark paper	Brittle bead; white crust	Volatilises and smells of garlic

Group III.—To O.S. add NH_4Cl in excess, and NH_4OH until the solution smells of ammonia. *You should let the mixture stand for at least two minutes before passing on to the next group, because ppts. in this group are frequently invisible at first.*

Experiment	Aluminium	Chromium	Iron (Ferrous)	Iron (Ferric)	Phosphate, etc.
NH_4OH ppt. is	White flocculent $Al(OH)_3$	Bluish-green $Cr(OH)_3$	Dirty green $Fe(OH)_2$	Reddish-brown $Fe(OH)_3$	White $Ca_3(PO_4)_2$, etc.
To O.S. add NaOH	White ppt. of $Al(OH)_3$, soluble in excess	Bluish-green ppt. of $Cr(OH)_3$	Green ppt. of $Fe(OH)_2$	Reddish-brown ppt. of $Fe(OH)_3$	White ppt. of $Ca_3(PO_4)_2$, etc., insoluble in excess
To O.S. add $K_4Fe(CN)_6$	——	——	White ppt. of $K_2Fe(CN)_6$; rapidly goes blue	Dark blue ppt. of Prussian blue, $Fe_7(CN)_{18}$	——
To O.S. add $K_3Fe(CN)_6$	——	——	Dark blue ppt. of Turnbull's blue, $Fe_3(CN)_{12}$	Reddish coloration	——
To O.S. add KCNS	——	——	——	Blood-red coloration	——
Borax bead	Colourless	Green	Green in reducing flame Reddish in oxidising flame		Colourless
Heat solid on charcoal with $Co(NO_3)_2$	Blue mass	Some green Cr_2O_3 *may* be formed	——	——	Blue mass in some cases

If a white precipitate, insoluble in excess, is obtained with NaOH, test as follows :—

(1) **Phosphate of Ca, Ba, Sr, or Mg**—Make a nitric acid solution of the original substance, add excess of ammonium molybdate solution and gently warm. A yellow ppt. indicates *phosphate*. If no ppt. is obtained, pass on to (2). If a yellow ppt. is produced, dissolve some of the original substance in the least possible quantity of HCl, add excess of sodium acetate solution, and a few drops of acetic acid. Add a few drops of $FeCl_3$. *A yellowish white ppt. confirms phosphate of Ca, Ba, Sr, or Mg*. If a ppt. is formed, add $FeCl_3$ until the solution is red. Boil. Add NH_4OH in excess. Filter, and test the filtrate for Groups IV, V and VI.

(2) **Oxalate of Ca, Ba, or Sr**—Heat the original substance to low redness, and add acetic acid to the cold residue. Effervescence indicates *oxalate*. Filter if necessary, and test the filtrate for Group V.

(3) **Fluoride, borate of Ca, Ba, or Sr**—Fuse the original substance with Na_2CO_3. Extract with water, filter, test the residue for Group V and the solution for fluoride and borate.

Group IV.—To solution from Group III, if NH_4Cl and NH_4OH have given no ppt., add a few drops of $(NH_4)_2S$ solution. NH_4Cl and NH_4OH must also be present.

Experiment	Zinc	Manganese	Cobalt	Nickel
Group ppt. is	White ZnS	Flesh-coloured MnS	Black CoS	Black NiS
To O.S. add NaOH	White ppt. of $Zn(OH)_2$	Dirty white ppt. of $Mn(OH)_2$	Blue ppt. of $Co(OH)_2$	Light green ppt. of $Ni(OH_2$
Borax bead	Colourless	Amethyst	Blue	Brownish)
Heat solid on charcoal with $Co(NO_3)_2$	Green mass	———	———	———

Group V.—To solution from Group IV, if $(NH_4)_2S$ has given no ppt., add $(NH_4)_2CO_3$ solution. NH_4Cl and NH_4OH must also be present.

Experiment	Barium	Strontium	Calcium
Group ppt. is	White $BaCO_3$	White $SrCO_3$	White $CaCO_3$
To O. S. add $CaSO_4$ solution	White ppt. of $BaSO_4$ immediately	White ppt. of $SrSO_4$ on standing for some time	———
Flame coloration	Green	Crimson	Red

Group VI.—Test separately for the metals in this group.

(1) To solution from Group V, if $(NH_4)_2CO_3$ has given no ppt., add Na_2HPO_4 solution. NH_4Cl and NH_4OH must also be present.

A *white ppt.* of $MgNH_4.PO_4$ indicates *magnesium.*

Confirm by heating the original solid on charcoal with $Co(NO_3)_2$. A *pink mass* confirms the presence of *magnesium.*

(2) Boil some of the original solid with NaOH solution, and test for ammonia by smell and litmus paper.

Evolution of *ammonia* indicates the presence of *ammonium.*

(3) Test for sodium and potassium by the flame test.

Yellow coloration invisible through blue glass indicates *sodium.*

Lilac coloration visible through blue glass indicates *potassium.*

Confirm the presence of potassium by making a strong solution of the original solid in water, and adding strong tartaric acid solution. A *white crystalline ppt.* of potassium hydrogen tartrate, when the solution is allowed to stand, indicates the presence of *potassium.*

PRELIMINARY EXAMINATION FOR ACID RADICLE

1. Treat the solid substance with dilute HCl in the cold. Afterwards heat.

Evolution in the cold of CO_2. (Test gas with lime-water)	Carbonate
,, ,, ,, Cl_2. (Test gas by smell and colour. It gives a blue colour with KI starch paper . .	Hypochlorite
,, ,, ,, oxides of nitrogen. (Recognise by smell and brown colour) .	Nitrite
Evolution of H_2S. (Gas blackens lead acetate paper)	Sulphide
,, SO_2. (Gas turns potassium bichromate green)	Sulphite
,, SO_2 and deposition of sulphur . .	Thiosulphate
,, HCN. (Gas is very poisonous and has a peculiar smell)	Cyanide

Before passing to the next test, test for *sulphide* by warming with *strong* HCl, because some sulphides are not decomposed by dilute HCl.

2. Heat the solid substance with strong H_2SO_4.

The above salts give the same results as with HCl.	With sulphuric acid there may be in addition—
Evolution of ClO_2. (Yellow explosive gas) . . .	Chlorate
,, oxides of nitrogen. (Yellow or brown gases with smell like that of strong nitric acid)	Nitrate or Nitrite
,, acetic acid. (Smells like vinegar) . .	Acetate
,, CO and CO_2. (The CO burns at mouth of tube with a blue flame. The CO_2 is detected with lime-water. No blackening)	Oxalate
,, CO. (No CO_2 and no blackening) . .	Ferrocyanide
,, CO, and liquid blackens quickly . .	Tartrate
,, CO, and liquid blackens slowly . .	Citrate
,, I_2. (Violet fumes and irritating smell) .	Iodide

Evolution of Br_2. (Brownish-red fumes with irritating smell; condense to red liquid in cold part of tube) . . . . . Bromide
" HCl. (Colourless gas; fumes strongly in air; irritating smell) . . . . Chloride
" SiF_4. (White fumes, which deposit gelatinous silica on a moist glass rod) . . Fluoride

EXAMINATION FOR ACID RADICLE

Make a solution of a small quantity of the solid by mixing it with at least twice as much solid Na_2CO_3, and boiling the mixture with a small quantity of water for some time. Filter. Add dilute HNO_3 to the solution until it is just acid. Warm gently to drive off CO_2.

Test portions of the solution as follows:—

Group I. Add dilute HCl, and barium chloride solution.

White ppt. of $BaSO_4$ indicates presence of *sulphate*.

Confirm by heating on charcoal with Na_2CO_3, placing the mass on a silver coin, and moistening with water.

A black stain on the coin confirms the presence of *sulphate*.

Group II. Add NH_4OH until alkaline, filter if necessary, and then add calcium chloride solution.

White ppt. of calcium salt indicates the presence of *oxalate, fluoride, phosphate, arsenate, borate, tartrate, citrate,* or *silicate*.

Warm the ppt. for some time with acetic acid.

Ppt. dissolved, indicates presence of *phosphate, arsenate, borate, tartrate,* or *citrate*.
Ppt. undissolved, " *oxalate* or *fluoride*.
Ppt. decomposed, " *silicate*.

Distinguishing tests—

Phosphate and *arsenate* give a yellow ppt. with nitric acid and ammonium molybdate on gentle warming.

Arsenate gives a yellow ppt. of As_2S_3 with H_2S on boiling the dilute solution and passing H_2S several times. *Phosphate does not do this.*

Borate with strong H_2SO_4 and alcohol in a porcelain dish gives a green-edged flame when the alcohol is lighted.

Tartrate with NaOH in excess and a few drops of potassium permanganate gives a green colour, which changes to a brown ppt. on heating.

Citrate with NaOH in excess and a few drops of potassium permanganate gives a green colour, which does not change on heating.

Oxalate with MnO_2 and strong H_2SO_4 gives CO_2 without heating.

Fluoride, heated with strong H_2SO_4, gives a greasy appearance in the tube and evolves fumes of SiF_4.

Group III.—To solution add dilute HNO_3 and $AgNO_3$ solution.

White ppt. of AgCl or AgCN, easily soluble in NH_4OH, indicates } *chloride* or *cyanide*

White ppt. of $Ag_4Fe(CN)_6$, insoluble in NH_4OH, indicates *ferrocyanide*
Yellowish-white ppt. of AgBr, slightly soluble in NH_4OH, indicates } *bromide*
Yellow ppt. of AgI, insoluble in NH_4OH, indicates *iodide*
Orange ppt. of $Ag_3Fe(CN)_6$, easily soluble in NH_4OH, indicates } *ferricyanide*
Crimson ppt. of Ag_2CrO_4, soluble in NH_4OH, indicates *chromate*
Black ppt. of Ag_2S, insoluble in NH_4OH, indicates *sulphide*

Distinguishing tests—

Chloride. Heat with MnO_2 and strong H_2SO_4. Chlorine evolved.
Cyanide. Add $FeSO_4$, $FeCl_3$, and strong HCl. Dark blue ppt. of Prussian blue.
Ferrocyanide. Add $FeCl_3$. Dark blue ppt. of Prussian blue.
Ferricyanide. Add $FeCl_3$. No ppt.
Bromide. Heat with MnO_2 and strong H_2SO_4. Bromine evolved.
Iodide. Heat with MnO_2 and strong H_2SO_4. Iodine evolved.

Group IV.—Add $FeCl_3$ to the neutral solution.

Blood-red colour, not bleached by dilute HCl, indicates *sulphocyanate*
Red colour, bleached by dilute HCl, indicates *acetate*
Red colour. Liquid shaken with carbon bisulphide colours the bisulphide violet. Indicates } *iodide*
Yellowish-white ppt. indicates } *phosphate* or *arsenate*

Group V.—Test specially for chromate.

(1) Lead acetate gives a yellow ppt. of $PbCrO_4$.
(2) Boil with alcohol and HCl. Yellow colour of the solution is changed to green, owing to reduction of the chromate to chromium salt.

Test original solution for nitrate.

(1) Add $FeSO_4$ solution to a cold solution of the nitrate in water. Pour strong H_2SO_4 gently down the side of the tube. A *brown ring* is produced at the surface of contact of the two liquids.
(2) Add H_2SO_4 and copper turnings and warm. If a nitrate is present, a blue solution and brown fumes of oxides of nitrogen are produced.

If no acid radicle has been found, test for oxide or hydroxide.

(1) Soluble oxides or hydroxides are alkaline to litmus, and they give a brown ppt. of Ag_2O with $AgNO_3$. The ppt. is soluble in NH_4OH or in acids.
(2) Insoluble oxides or hydroxides must be compared with the oxide and hydroxide of the metal found in the analysis for base.

EXPLANATION OF THE ANALYTICAL TABLES

Preliminary Examination for base.

(1) The yellow sublimate is sulphur; the white sublimate may be any volatile salt of NH_4, Hg, Sb, or As.
(2) Sodium carbonate acts like caustic soda towards ammonium salts,

and sets free ammonia. Charcoal reduces to the metal, arsenic and mercury oxides, produced by the interaction of the metallic compound with Na_2CO_3.

(3) The residue, which is yellow while hot and white when cold, is zinc oxide, ZnO. The green mass is chromium oxide, Cr_2O_3.

(4) The various coloured masses obtained are compounds of the oxides of the metals with cobalt oxide.

(5) The Na_2CO_3 acts mainly as a flux. It brings the compound of the metal into close contact with the hot charcoal. The KCN is a powerful reducing agent, owing to the ease with which it takes up oxygen to form KCNO. The incrustations produced are oxides, obtained by the partial burning of the metal after it has been formed from its salts.

(6) Borax, when heated, first swells up and loses its water of crystallisation, and then forms a colourless glass consisting of boron oxide, B_2O_3, and sodium metaborate, $NaBO_2$.

$$Na_2B_4O_7.10H_2O = 2NaBO_2 + B_2O_3 + 10H_2O$$

The metallic salts introduced are converted at the high temperature of the bead to oxides, which dissolve in the molten borax, forming coloured glasses.

(7) The substance is moistened with strong hydrochloric acid, because the chlorides of many metals are their most volatile salts.

Solution of salt.

A fairly dilute solution should be used for analysis with the ordinary tables. A strong solution of barium chloride would give a ppt. of $BaCl_2$ in Group I, owing to the insolubility of $BaCl_2$ in hydrochloric acid.

Dilute hydrochloric acid dissolves most of the salts which are insoluble in water. It is a more useful solvent than dilute nitric acid, because the latter causes a considerable deposition of sulphur in Group II, which may mask a true precipitate. A solution in strong nitric acid or aqua regia should be evaporated to get rid of the acid. The acid would cause deposition of sulphur in Group II, and if neutralised with NaOH or NH_4OH, would affect the solubility of some precipitates by reason of the strong solution of sodium or ammonium salts produced. Aqua regia produces chlorides of the metals dissolved.

The fusion with sodium carbonate produces insoluble carbonates or oxides of the metals, and a soluble sodium salt of the acid.

$$\underset{\text{Insoluble}}{BaSO_4} + Na_2CO_3 = \underset{\text{Soluble in HCl}}{BaCO_3} + Na_2SO_4$$

$$\underset{\text{Insoluble}}{CaF_2} + Na_2CO_3 = \underset{\text{Soluble in HCl}}{CaCO_3} + 2NaF$$

Separation of metals into groups.

I. A small group of three metals is obtained by addition of dilute HCl to a cold solution of the salt. Only lead, mercurous and silver salts form insoluble chlorides. No ppt. on addition of HCl indicates therefore the absence of these metals. The chloride of lead is somewhat soluble in cold water, and therefore lead is included in Group II.

II. A number of the remaining metals form sulphides, which are insoluble in dilute acids. Of these sulphides, PbS, CuS, Bi_2S_3, HgS, and

CdS are insoluble in ammonium sulphide, and SnS, SnS_2, Sb_2S_3, and As_2S_3, are soluble in ammonium sulphide with formation of double sulphides. By means of ammonium sulphide, therefore, the large group of nine can be split up into the two more workable groups of five and four metals. No precipitate with H_2S therefore indicates the absence of lead, copper, bismuth, mercury, cadmium, tin, antimony, and arsenic.

Repeated boiling and saturation with H_2S are necessary in order to ensure the precipitation of arsenic. Arsenic compounds are thus reduced to arsenious compounds, which are precipitated by the H_2S. The dilution of the solution, after passage of H_2S, is necessary to ensure precipitation of some solutions of cadmium and lead, the sulphides being formed only in presence of very dilute acid.

Marsh's test—If a solution of arsenic or antimony is placed in a flask, together with zinc (free from arsenic) and dilute HCl, a mixture of hydrogen with arsine AsH_3 or stibine SbH_3 is evolved. The arsenic or antimony solution is usually put into the flask when the hydrogen has been coming off for some time and has been lighted at a jet. The hydrogen must be tested before a light is applied by filling a test-tube by upward displacement of air. If the hydrogen in the tube burns quietly, the jet may be lighted with safety. A cold porcelain lid or porcelain dish is held against the flame after the addition of the arsenic or antimony solution. The black stain produced is a metallic soot of arsenic or antimony, caused by the decomposition of the evolved hydrides by the heat of the flame.

III. From the remaining metals a small group of three can be separated by taking advantage of the insolubility of the hydroxides of aluminium, chromium, and iron in ammonium chloride solution. Some of the other remaining metals form hydroxides insoluble in NH_4OH, but these are soluble in ammonium chloride solution. Excess of ammonium chloride must therefore be added before the addition of ammonium hydroxide.

The phosphates, borates, oxalates, and fluorides of Mg, Ca, Ba, and Sr are soluble in dilute acids. Therefore, on addition of NH_4OH, they may be precipitated, owing to neutralisation of the acid holding them in solution.

Phosphate is removed by boiling with ferric chloride, when ferric phosphate is precipitated, and the chloride of Ca, Ba, Sr, or Mg remains in solution. The excess of $FeCl_3$ is removed as $Fe(OH)_3$ by addition of NH_4OH.

Oxalates are converted to carbonates by strong heating. The carbonates of Mg, Ca, Ba, or Sr are readily soluble in acetic acid.

Fluorides and borates, when fused with sodium carbonate, give oxide or carbonate of the metal, and sodium fluoride or borate. The fluoride and borate are dissolved out with water. The oxide or carbonate of the metal is dissolved in dilute acid and tested for metals of Groups V and VI.

IV. Ammonium sulphide in alkaline solution precipitates sulphides of zinc, manganese, nickel, and cobalt. Many other metals in the preceding groups would also give insoluble sulphides, but their absence has already been proved. The NH_4Cl is added to prevent the precipita-

tion of the hydroxides which would be formed when NH_4OH is added to make the solution alkaline.

V. Here again an alkaline solution is necessary. It is obtained by means of NH_4Cl and NH_4OH.

The precipitation of strontium sulphate by means of $CaSO_4$ solution may be hastened by rubbing the inside of the test-tube, above and below the level of the liquid with a glass rod.

VI. All ammonium salts readily give off ammonia when boiled with NaOH.

$$NH_4Cl + NaOH = NaCl + NH_3 + H_2O$$

Tartaric acid gives a ppt. only with strong solutions of potassium salts, because potassium hydrogen tartrate is slightly soluble in water

Preliminary examination for acid radicle.

The blackening of lead acetate paper by H_2S is due to the formation of lead sulphide, PbS.

Sulphur dioxide reduces potassium bichromate to a green chromium salt.

Silicon fluoride, SiF_4, is obtained by the action of the hydrofluoric acid, HF (which is set free from a fluoride by sulphuric acid), with the silica of the glass of the test-tube.

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

The gelatinous silica deposited on the wet glass rod is obtained from the decomposition of the SiF_4 by water.

$$3SiF_4 + 4H_2O = \underset{\text{Hydro-fluo-silicic acid}}{2H_2SiF_6} + \underset{\text{Gelatinous silica}}{SiO_2.2H_2O}$$

Examination for acid radicle.

The boiling of the salt with strong Na_2CO_3 solution causes the precipitation of insoluble carbonates or hydroxides of most metals, and the formation of the soluble sodium salts of the acid radicles. Thus—

$$CaSO_4 + Na_2CO_3 = \underset{\text{In solution}}{Na_2SO_4} + \underset{\text{Precipitated}}{CaCO_3}$$

It must be remembered that the solution, after acidification with nitric acid, contains nitrate, and therefore must not be tested for nitrate.

I. Hydrochloric acid is added in order to prevent the precipitation of barium salts, which are insoluble in water. $BaSO_4$ is insoluble in the acid. Barium silico-fluoride, $BaSiF_6$, is also insoluble in the acid and may be precipitated in this group.

Sulphates, heated on charcoal with Na_2CO_3, are reduced by the charcoal to sulphides, which react with the Na_2CO_3, forming some sodium sulphide, Na_2S. The solution of sodium sulphide in water forms silver sulphide with metallic silver.

$$CaSO_4 + 4C = CaS + 4CO$$
$$CaS + Na_2CO_3 = CaCO_3 + Na_2S$$

II. The green-edged flame, obtained in the confirmatory test for

borate is caused by the volatile boracic acid set free by the sulphuric acid from the borate. The confirmatory test for tartrate with potassium permanganate, $KMnO_4$, is valuable only when tartrate or citrate has been shown to be present by the preliminary examination with sulphuric acid.

The reaction of oxalates with MnO_2 and strong H_2SO_4 is—

$$Na_2C_2O_4+MnO_2+2H_2SO_4=Na_2SO_4+2CO_2+MnSO_4+2H_2O$$

III. The crimson precipitate of silver chromate, Ag_2CrO_4, is obtained only with strong solutions of chromates.

The reactions, by which Prussian blue can be obtained from a cyanide, may be represented by the following equations :—

$2KCN+FeSO_4=K_2SO_4+Fe(CN)_2$ Ferrous cyanide
$Fe(CN)_2+4KCN=K_4Fe(CN)_6$ Potassium ferrocyanide
$3K_4Fe(CN)_6+4FeCl_3=12KCl+Fe_7(CN)_{18}$ Prussian blue

The hydrochloric acid is added to ensure the acidity of the solution.

IV. The brown ring obtained in testing for nitrate is caused by the setting free of nitric acid by means of the sulphuric acid. The nitric acid is reduced to nitric oxide by the ferrous sulphate solution. The nitric oxide dissolves in more ferrous sulphate solution, forming a brown ring of $FeSO_4.NO$ at the surface of contact of the liquids.

$$2HNO_3+6FeSO_4+3H_2SO_4=3Fe_2(SO_4)_3+4H_2O+2NO$$

In the second test for nitrate, the nitric acid set free by the sulphuric acid attacks the copper, with formation of a blue solution of copper nitrate and evolution of oxides of nitrogen.

APPENDIX II

TABLE OF WATER VAPOUR PRESSURES

Temp.	Mm. of Mercury	Temp.	Mm. of Mercury	Temp.	Mm. of Mercury	Temp.	Mm. of Mercury	Temp.	Mm. of Mercury
° C.		° C.		° C.		° C.		° C.	
0	4.6	6	7.0	12	10.5	18	15.4	24	22.2
1	4.9	7	7.5	13	11.2	19	16.4	25	23.6
2	5.3	8	8.0	14	11.9	20	17.4	26	25.0
3	5.7	9	8.6	15	12.7	21	18.5	27	26.5
4	6.1	10	9.2	16	13.5	22	19.7	28	28.1
5	6.5	11	9.8	17	14.4	23	20.9	29	29.8

APPENDIX III

TABLE OF APPROXIMATE AND ACCURATE ATOMIC WEIGHTS *

The names of the elements studied in this book are printed in capitals.

NAME	Symbol	Approximate Atomic Weight O = 16	Accurate Atomic Weight H = 1	NAME	Symbol	Approximate Atomic Weight O = 16	Accurate Atomic Weight H = 1
Aluminium	Al	27	26.91	Molybdenum	Mo	96	95.26
Antimony (*Stibium*)	Sb	120	119.52	Neodymium	Nd	141	139.70
Argon	A	40	40.0	Nickel	Ni	59	58.24
Arsenic	As	75	74.44	NITROGEN	N	14	13.93
Barium	Ba	137	136.39	Osmium	Os	191	189.55
Beryllium (*Glucinum*)	Be	9	9.01	OXYGEN	O	16	15.88
Bismuth	Bi	208	206.54	Palladium	Pd	106	105.56
Boron	B	11	10.86	PHOSPHORUS	P	31	30.79
BROMINE	Br	80	79.34	Platinum	Pt	195	193.41
Cadmium	Cd	112	111.10	Potassium (*Kalium*)	K	39	38.82
Cæsium	Cs	133	131.89	Praseodymium	Pr	144	142.50
CALCIUM	Ca	40	39.76	Rhodium	Rh	103	102.23
CARBON	C	12	11.92	Rubidium	Rb	85	84.78
Cerium	Ce	140	139.10	Ruthenium	Ru	102	100.91
CHLORINE	Cl	35.5	35.18	Samarium	Sm	150	149.13
Chromium	Cr	52	51.74	Scandium	Sc	44	43.78
Cobalt	Co	59	58.49	Selenium	Se	79	78.42
Columbium (*Niobium*)	Nb	94	93.02	Silicon	Si	28	28.18
COPPER (*Cuprum*)	Cu	63	63.12	Silver (*Argentum*)	Ag	108	107.11
Erbium	Er	166	165.06	SODIUM (*Natrium*)	Na	23	22.88
FLUORINE	F	19	18.91	Strontium	Sr	88	86.95
Gadolinium	Gd	157	155.57	SULPHUR	S	32	31.83
Gallium	Ga	70	69.38	Tantalum	Ta	183	181.45
Germanium	Ge	72	71.93	Tellurium	Te	127	126.52
Gold (*Aurum*)	Au	197	195.74	Terbium	Tb	160	158.80
Helium	He	4	4.0(?)	Thallium	Tl	204	202.61
HYDROGEN	H	1	1.00	Thorium	Th	233	230.87
Indium	In	114	112.99	Thulium	Tm	171	169.40
IODINE	I	127	125.89	TIN (*Stannum*)	Sn	119	118.15
Iridium	Ir	193	191.66	Titanium	Ti	48	47.79
IRON (*Ferrum*)	Fe	56	55.60	Tungsten (*Wolfram*)	W	185	183.43
Lanthanum	La	139	137.59	Uranium	U	240	237.77
LEAD (*Plumbum*)	Pb	207	205.36	Vanadium	V	51	50.99
Lithium	Li	7	6.97	Ytterbium	Yb	173	171.88
Magnesium	Mg	24	24.10	Yttrium	Yt	89	88.35
Manganese	Mn	55	54.57	ZINC	Zn	65	64.91
Mercury (*Hydrargyrum*)	Hg	200	198.49	Zirconium	Zr	90	89.72

* The accurate atomic weights are the recalculated atomic weights of F. W. Clarke. See *Constants of Nature*, Part V, 1897

QUESTIONS

1. Explain the terms—solubility, saturated solution, efflorescence, sublimate.

2. How would you find the percentage of sal ammoniac in a mixture of salt and sal ammoniac?

3. What are the chief differences between acids and alkalis?

4. How would you prove that carbon dioxide contains carbon?

5. To the presence of what substances in water is temporary hardness due? How can permanent hardness be removed?

6. Describe an experiment which shows that air can be burned in coal gas.

7. Draw and describe the Davy lamp.

8. How would you prove that hydrochloric acid contains hydrogen and chlorine?

9. Describe and explain an apparatus that can be used for determining the weight of a litre of a gas.

10. A gas has a volume of 200 c.c. at 0° C. and 760 mm. What is its volume at 17° C. and 700 mm.?

11. Calculate the volume which 150 c.c. of hydrogen measured at 9° C. and 740 mm. pressure would occupy at 0° C. and 760 mm.

12. Find the volume of hydrogen at 11° C. and 770 mm. that can be obtained from 20 grams of water.

13. What weight of sulphur would it be necessary to burn in order to obtain 10 litres of sulphur dioxide measured at 10° C. and 800 mm. pressure?

14. Calculate the volume of carbon dioxide measured at 0° C. and 720 mm. which can be obtained from 20 grams of chalk.

15. .2 gram of a metal was dissolved in hydrochloric acid, and the hydrogen evolved was found to measure 85 c.c. at 12° C. and 764 mm. Calculate the equivalent weight of the metal.

16. 1.52 grams of a metallic oxide were reduced in a current of hydrogen, and 1.23 grams of the metal were obtained. Calculate the equivalent of the metal.

17. 2 grams of zinc were found to displace from a solution of a metallic salt 1.92 grams of the metal of the salt. Calculate the equivalent of the metal. The equivalent of zinc is 32.5.

18. Calculate the percentage composition of the following compounds:

sulphuric acid, ammonia, acetic acid, sodium bicarbonate, and cane sugar.

19. Find the formula of a substance containing 39.56 parts of carbon, 7.69 parts of hydrogen, and 52.75 parts of oxygen.

20. A substance contains 52.08 parts of carbon, 13.13 parts of hydrogen, and 34.79 parts of oxygen. (The vapour density of the compound is 23.) Find the formula of the compound.

21. .3 gram of a volatile liquid, when converted into vapour in a Victor Meyer's apparatus, displaced 52 c.c. of air measured at 12° C. and 750 mm. Calculate the molecular weight of the volatile liquid.

22. .35 gram of a solid when dissolved in 25 grams of benzene lowered the freezing-point of the benzene by .33° C. Find the molecular weight of the solid. The constant for benzene is 49.

23. A lowering of freezing-point of 1° C. was caused by the solution of 1.5 grams of a solid in 30 grams of water. Find the molecular weight of the solid. The constant for water is 19.

24. .42 of a metal when dissolved in hydrochloric acid sets free .053 gram of hydrogen. The metal is a diad. Find its atomic weight.

25. State Dulong and Petit's Law.

3.414 grams of a metallic oxide when reduced to metal produced 2.957 grams of metal. The specific heat of the metal is .032. Calculate the accurate atomic weight of the metal.

26. Describe experiments which illustrate Graham's Law of Diffusion.

27. Compare the properties of water and hydrogen peroxide. How many c.c. of oxygen at 0° C. and 760 mm. could be obtained by heating 100 c.c. of a solution of hydrogen peroxide containing 20 grams of the peroxide per litre of solution?

28. 2.733 grams of a crystalline salt when heated strongly lost 1.400 grams of water. The molecular weight of the anhydrous salt is 120. Calculate the number of molecules of water of crystallisation in the salt.

29. Compare the properties of oxygen and ozone.

30. 10 c.c. of normal caustic soda solution required for neutralisation 11.4 c.c. of a solution of hydrochloric acid. Calculate the number of grams of hydrochloric acid in one litre of the solution.

31. 100 c.c. of normal caustic soda solution were added to 20 c.c. of copper sulphate solution, and the liquid was well mixed and filtered. 10 c.c of the filtrate required 6.4 c.c. of normal sulphuric acid to neutralise it. Find the weight of anhydrous copper sulphate in 1 c.c. of the copper sulphate solution.

32. .5 gram of iron wire was dissolved in dilute sulphuric acid, and the solution was made up to 500 c.c. 50 c.c. of the ferrous sulphate solution was found to decolorise 8.2 c.c. of decinormal potassium permanganate solution. Calculate the percentage impurity in the iron.

33. Define "solubility." How would you find the solubility of magnesium sulphate at 40° C.?

34. Gunpowder is a mixture of saltpetre, sulphur, and charcoal. How would you obtain from gunpowder pure specimens of these substances ?

35. What method would you use to prepare a pure specimen of common salt from a mixture of common salt, sal ammoniac, and chalk ?

36. Describe the effect of heating in hard glass test-tubes the following substances : (*a*) alum, (*b*) copper sulphate, (*c*) ferrous sulphate, (*d*) common salt, (*e*) sal ammoniac, (*f*) iodine.

37. If you were given a quantity of a clear liquid, what experiments would you carry out in order to find if the liquid was water ?

38. What experiments could you make to find out if the presence of common salt dissolved in water prevents the water from lathering freely with soap ?

39. Describe what happens when the following substances are heated (*a*) in a tube closed at one end, (*b*) on an iron spoon : copper, magnesium, lead, zinc, sulphur, charcoal. Account for the different actions in (*a*) and (*b*) as well as you can.

40. How would you prove that the presence of water is necessary for the rusting of iron in air ? Draw the apparatus you would use.

41. Suggest a method that could be used for finding the weight of a litre of a gas which is very soluble in water.

42. Show clearly how Lavoisier's experiment disproved the Phlogistic Theory.

43. Make drawings of the apparatus that could be used in obtaining hydrogen from water by two different methods. Describe the manner in which each method is carried out.

44. Make a table showing which of the following metals produce hydrogen when treated with (*a*) hydrochloric acid, (*b*) nitric acid, and (*c*) sulphuric acid : iron, copper, lead, tin, zinc, magnesium, aluminium.

45. Make a list of the properties of hydrogen.

46. Describe an experiment which proves that water is formed when hydrogen is burnt in air.

47. What are the differences between (*a*) chemical compounds and mechanical mixtures, (*b*) physical change and chemical change ? Illustrate your answer by means of examples.

48. How did Lavoisier prove that matter cannot be destroyed ?

49. How would you prove by means of experiment that charcoal and graphite are the same substance in different forms ?

50. Describe a method you could use to find the percentage of carbon dioxide in magnesium carbonate.

51. How would you find the weight of carbon dioxide that could be obtained from 1 gram of carbon ?

52. When the apparatus, Fig. 32, is used, some carbon dioxide is dissolved by the hydrochloric acid solution, and a considerable error is thereby produced. What modification in the method would you make in order to avoid this error ?

53. How would you convert in the laboratory (*a*) limestone into lime, (*b*) lime into calcium carbonate, (*c*) a mixture of sodium carbonate and lime into pure specimens of calcium carbonate and caustic soda ? Give full details of the apparatus and method you would use.

54. Write an account of the chief chemical changes which take place in the breathing of animals. In what ways does breathing resemble burning ?

55. Draw the flame of a bunsen burner (*a*) with the holes at the base open, (*b*) with the holes closed. Mention the differences in the two flames, and explain the differences as well as you can.

56. Describe what happens when hydrochloric acid solution is added to (*a*) sodium carbonate, (*b*) lime, (*c*) silver nitrate solution, (*d*) zinc.

57. What gas is obtained when hydrochloric acid gas is passed over heated lead peroxide ? What takes place if (1) powdered antimony, (2) yellow phosphorus, (3) filter paper moistened with turpentine, are put into jars of this gas ?

58. Reduce the following volumes to 0° C. and 760 mm. pressure : (*a*) 250 c.c. at 11° C. and 740 mm., (*b*) 700 c.c. at 50° C. and 770 mm., (*c*) 50 c.c. at 25° C. and 400 mm., (*d*) 100 c.c. at 157° C. and 1020 mm. pressure.

59. 70 c.c. of hydrogen, collected over water, were found to be at a temperature of 15° C. and a pressure of 749 mm. The pressure of water vapour at 15° C. is equal to that of 12.7 mm. of mercury. Find the volume of the dry gas at 0° C. and 760 mm. pressure.

60. A tube, A, containing dry oxygen, collected over dry mercury, was found to contain 50 c.c. of the gas at a temperature of 12° C. and a pressure of 750 mm. Another tube of oxygen, B, collected over water, was found to contain 51 c.c. at the same temperature and pressure. Which tube contains the greater quantity of oxygen ? (Pressure of aqueous vapour at 12° C. = 10.5 mm.)

61. If a solution of common salt is treated with silver nitrate solution all the chlorine in the salt is precipitated as insoluble silver chloride How would you make common salt in two different ways, and prove that the salt obtained by both methods has the same composition ?

62. Three samples of lead monoxide were prepared in three different ways—(*a*), (*b*), and (*c*). The lead monoxide in each case was reduced to lead by heating in a stream of hydrogen. The results of these operations were—

(*a*)	3.18	grams of	monoxide	produced	2.95	grams of	lead	
(*b*)	2.48	,,	,,	,,	2.30	,,	,,	,,
(*c*)	2.02	,,	,,	,,	1.88	,,	,,	,,

Are these results in accordance with the law of Constant Proportions ?

63. The chlorides of lead have the following percentage composition—

(*a*)		(*b*)	
Lead	= 74.2	Lead	= 59.3
Chlorine	= 25.7	Chlorine	= 40.7

Show that these numbers are in agreement with the law of Multiple Proportions.

64. The two oxides of tin have the percentage composition—

(*a*)		(*b*)	
Tin	= 88.2	Tin	= 78.8
Oxygen	= 11.8	Oxygen	= 21.2

Are these numbers in agreement with the law of Multiple Proportions ?

65. How would you determine the equivalent weight of aluminium ?

66. .3 gram of a metal displaced 90 c.c. of hydrogen measured at 14° C. and 745 mm. pressure. The hydrogen was collected over water Find the equivalent weight of the metal.

67. Hydrogen was passed over the heated oxide of a metal and the water produced was collected in a calcium chloride tube. The oxide was completely reduced to metal. The weight of the oxide was 1.45 grams and the weight of the water produced was .56 gram. Calculate the equivalent weight of the metal, assuming the composition of water to be known.

68. Equal weights of two metals were dissolved separately in hydrochloric acid. The hydrogen obtained from metal A, which had an equivalent weight of 26.5, measured 145 c.c. at 15° C. and 750 mm. pressure. The hydrogen from B measured 120 c.c. at 16° C. and 750 mm. pressure. Find the equivalent weight of the metal B.

69. 1 gram of metallic iron was converted into anhydrous ferrous chloride, and a second gram of the metal was converted into anhydrous ferric chloride. The weights of ferrous chloride and ferric chloride produced were respectively 2.27 and 2.90 grams. Calculate the two equivalent weights of iron. The equivalent weight of chlorine is 35.5.

70. .35 gram of a metal was converted completely into the oxide of the metal. The oxide weighted .43 gram. What is the equivalent weight of the metal ? Calculate the weight of sulphuric acid which would be necessary to dissolve the oxide produced.

71. A metal, A, produced, when oxidised, 1.25 grams of metallic oxide and an equal weight of a metal, B, produced 1.21 grams of metallic oxide. If the equivalent weight of B is 36, what is the equivalent weight of A ?

72. Equal weights of zinc, put into solutions of the sulphates of two metals, X and Y, set free .53 gram of X and .94 gram of Y. The equivalent weight of Y is 64. What is the equivalent weight of X ?

73. 500 c.c. of dry chlorine measured at 12° C. and 735 mm. pressure were passed into a solution of potassium iodide. 5.28 grams of iodine were set free. The equivalent weight of chlorine is 35.5. 1 litre of dry chlorine at N.T.P. weighs 3.18 grams. Calculate the equivalent weight of iodine.

74. Find the weight of crystallised ferrous sulphate ($FeSO_4.7H_2O$) that can be obtained from 1 gram of iron.

75. Calculate the weight of zinc which would be required to produce 10 grams of anhydrous zinc chloride ($ZnCl_2$).

76. What weight of manganese dioxide is required to produce 15 litres of dry chlorine measured at 10° C. and 750 mm. pressure ?

77. What volume of hydrogen measured at N.T.P. is required to reduce 5 grams of lead monoxide to metallic lead ?

78. Calculate the percentage composition of the following compounds: (*a*) anhydrous copper sulphate, (*b*) crystallised zinc sulphate, (*c*) ammonium chloride, (*d*) silver nitrate, (*e*) orthophosphoric acid.

79. Find the formula of a substance containing carbon 74.07 per cent., hydrogen 8.64 per cent., and nitrogen 17.29 per cent.

80. A substance has the percentage composition—carbon = 68.8, hydrogen = 4.92, oxygen = 26.25. Find the formula of the substance.

81. A substance has the percentage composition—carbon = 15.84, hydrogen = 2.20, nitrogen = 18.52, oxygen = 63.50. Find the formula of the substance.

82. A crystalline specimen of cobalt iodide contained 18.70 per cent. of water. Anhydrous cobalt iodide has the formula CoI_2. Find the simplest formula for the specimen.

83. .25 gram of a volatile liquid, when converted into vapour in a Victor Meyer's apparatus, displaced 72 c.c. of air measured over water at 15° C. and 742.7 mm. pressure. Find the molecular weight of the volatile liquid.

84. .54 gram of a volatile liquid expelled, when the liquid was dropped into a Victor Meyer tube, 60 c.c. of air. The air was collected and measured over dry mercury at 10° C. and 750 mm. pressure. What is the molecular weight of the volatile liquid.

85. .18 gram of an organic compound, when dissolved in 25 grams of benzene, lowered the freezing-point of the benzene .27° C. The constant for benzene is 49. Find the molecular weight of the organic compound.

86. A substance has a molecular weight of 150. What lowering of freezing-point will be produced in 28 grams of pure acetic acid by solution in the acid of 1 gram of the substance ? Constant for acetic acid = 39.

87. When two grams of an organic compound of molecular weight 120 were dissolved in 20 grams of a solvent, a lowering of 2.3° C. was produced in the freezing-point of the solvent. Calculate the constant for the solvent.

88. 2.59 grams of a metallic chloride produce on complete reduction 1.07 grams of the metal. The specific heat of the metal is .087. What is the accurate atomic weight of the metal ?

89. 1 gram of a triad metal, when completely oxidised, produced 1.2 grams of oxide. Calculate (*a*) the equivalent weight of the metal, (*b*) the accurate atomic weight of the metal, and (*c*) the specific heat of the metal.

90. .21 gram of a metal, when dissolved in hydrochloric acid, set free 115 c.c. of dry hydrogen measured at 0° C. and 760 mm. pressure. Assuming that 1 litre of dry hydrogen at N.T.P. weighs .09 grams, and that the specific heat of the metal is .161, calculate the accurate atomic weight of the metal.

91. 15.4 c.c. of decinormal sulphuric acid solution were required to neutralise 10 c.c. of a solution of sodium carbonate. Calculate the number of grams of sodium carbonate in 1 c.c. of the solution of carbonate.

92. 10 c.c. of normal caustic soda solution were neutralised by 8.4 c.c. of a solution of oxalic acid. Calculate the number of c.c. of water which must be added to a litre of the oxalic acid solution to make the latter of normal strength.

93. Calculate the number of c.c. of water which it is necessary to add to 100 c.c. of a caustic soda solution containing .472 gram of NaOH in order to make the caustic soda solution of decinormal strength.

94. 200 c.c. of $\frac{N}{10}$ Na_2CO_3 solution were added to 50 c.c. of a solution of barium chloride. The mixture was thoroughly shaken and allowed to stand until the precipitated barium carbonate had settled. It was found that 20 c.c. of the clear liquid above the precipitate required 9.5 c.c. of $\frac{N}{10}$ HCl solution to neutralise them. Calculate the weight of anhydrous barium chloride dissolved in 1 c.c. of the barium chloride solution.

95. .4 gram of a metal was dissolved in 100 c.c. of normal sulphuric acid. After the solution was complete, it was found that 20 c.c. of the acid liquid were neutralised by 11.2 c.c. of normal caustic soda solution. Calculate the chemical equivalent of the metal.

96. 1.5 grams of iron were dissolved in 50 c.c. of bench dilute sulphuric acid, the solution was diluted to 250 c.c., and 10 c.c. of the diluted solution was titrated with normal caustic potash solution. 8 c.c. of the caustic potash solution was used. Another 50 c.c. of bench dilute sulphuric acid was diluted to 250 c.c. 10 c.c. of this acid required 10.1 c.c. of normal caustic potash solution to neutralise it. Calculate the chemical equivalent of iron.

97. 1 gram of a base, insoluble in water, was dissolved into 100 c.c. of normal hydrochloric acid, and the acid liquid obtained was titrated against normal caustic soda. 10 c.c. of caustic soda were neutralised by 11.6 c.c. of the acid liquid. Calculate the equivalent of the base.

98. 10 c.c. of a ferrous sulphate solution required 12.5 c.c. of decinormal potassium permanganate solution to completely oxidise the iron to the ferric state. Calculate the weight of ferrous iron in 100 c.c. of the ferrous sulphate solution.

99. 20 c.c. of a solution of a mixture of ferrous sulphate and ferric sulphate required 8.5 c.c. of decinormal potassium permanganate to completely oxidise it. 100 c.c. of the mixture was reduced by means of zinc and dilute sulphuric acid until no ferric sulphate remained. The solution was then washed into a 500 c.c. measuring flask and the volume made up to 500 c.c. with distilled water. 50 c.c. of this solution required 9.8 c.c. of decinormal potassium permanganate to oxidise the ferrous to ferric iron. Calculate the weights of ferrous iron and ferric iron present in 100 c.c. of the original mixture.

100. 10 c.c. of a solution of oxalic acid was completely oxidised by 13.6 c.c. of decinormal potassium permanganate solution. Calculate the weight of oxalic acid ($H_2C_2O_4$) in a litre of the solution.

QUESTIONS SET IN THE LONDON MATRICULATION EXAMINATION

1. What simple relationship has been found to exist between the volumes of gases which take part in a chemical change? Describe an experiment illustrating this. What volume of air containing 21 per cent. of oxygen would be needed for the complete combustion of 15 litres of acetylene?

2. To what common chemical substances are the terms "acid" and "base" respectively applied? What do you understand by these terms? What bodies are formed by the interaction of an acid and a base? How would you proceed in the case of a given acid—say sulphuric acid—to determine by experiments whether only one such body or more than one can be obtained by interaction with a given alkali—such as potash?

3. When a piece of sulphur is burnt in air it disappears. How would you prove that it is not really destroyed? How would you show that a portion of the air only is concerned in the burning? Draw carefully the apparatus you would use.

4. How would you prepare and collect a jar of dry ammonia? Make a careful drawing of the apparatus you would use. What experiments would you make to show (1) that ammonia dissolves with extreme readiness in water, (2) that it contains both nitrogen and hydrogen?

5. Describe what you see and give the names of the substances formed when strong sulphuric acid is slowly poured over common salt. How would you obtain each product in a pure state? Draw carefully the apparatus you would use. What would you do to find out which of the products contains the chlorine of the salt?

6. Starting with iron filings, powdered sulphur, and concentrated sulphuric acid, describe exactly how you would proceed in order to prepare and collect a few jars of hydrogen sulphide. What compounds are produced when the gas burns freely in air? What is noticed when a light is applied to the mouth of a jar of the gas?

7. Describe the method you would follow in the laboratory in order to determine the proportion in which copper and oxygen combine to form the black oxide of copper. Supposing that by such an experiment you have found that 1.113 grams of copper combine with .280 grams of oxygen, calculate the equivalent of copper.

8. When oxalic acid is gently heated with oil of vitriol a mixture of the two oxides of carbon is obtained. How would you find by experiment the proportion in which the two oxides are mixed, and how could you separate them so as to obtain a quantity of each in a state of purity? Draw carefully the apparatus you would use.

9. What experiments would you make in order to investigate the truth of the following statement: "Nitre is more soluble in hot than in cold water, but oxygen is less soluble"?

10. How would you determine by experiment the volume of carbon dioxide given off when one gram of pure calcium carbonate is decomposed by an acid? Draw carefully the apparatus you would use.

11. Calculate the volume of carbon dioxide measured at 15° C. and 744 mm. pressure which should be obtained from 1.86 grams of calcium carbonate. [O=16, C=12, Ca=40; 1 litre of hydrogen at 0° C. and 760 mm. weighs 0.09 gram.]

12. Mention four common gases which burn in air with pale blue, feebly luminous flames. If a quantity of such a gas were given to you, how would you proceed to find out which of the four it might be?

13. When ammonium nitrate is heated, a gas is obtained which contains nitrogen and oxygen in the proportion of two volumes of nitrogen to one volume of oxygen. Why do we consider that in this gas the elements are present in a state entirely different from that in which they occur in air?

14. Describe carefully what can be observed when copper turnings are heated with strong sulphuric acid in a flask. How would you proceed in order to obtain crystals of copper sulphate from the contents of the flask at the end of the reaction? How could you recover some of the copper in the metallic state from these crystals?

15. The poles of a battery of several cells are attached to platinum electrodes which are dipped successively into (i) pure water, (ii) dilute sulphuric acid, (iii) a saturated solution of sodium chloride. State and explain what happens in each case. Draw carefully the apparatus you would use, showing the construction of the battery and the method of connecting the several parts of the apparatus.

16. Describe some experiments which illustrate the difference in properties between a vegetable oil, such as olive oil, and a mineral oil, such as petroleum.

17. Describe any two simple experiments which may be carried out in the laboratory and which illustrate the following statement :—

"However any given chemical compound is prepared, it is always found to be composed of the same elements combined in the same proportions."

18. Describe experiments which show that calcium carbonate contains the element carbon.

Ten grams of marble were placed in 100 c.c. of a warm solution of hydrogen chloride in water. When action had entirely ceased the residue of marble was removed and dried. It was then found to weigh 6 grams. From these data calculate the concentration of the acid in grams of hydrogen chloride per litre. [Ca=40, Cl=35.5.]

19. How are the two oxides of hydrogen prepared? What is the effect of heating each of them? Describe two experiments which illustrate the difference in chemical behaviour of these two substances.

20. Write full accounts of any two experiments you may have seen or made, which show that when a solid has been dissolved it is not always possible to recover the solid unchanged by evaporating the solution. Explain clearly the reason for this in each of the two cases you select.

21. What is the chemical nature of "washing soda"? How would you prepare a small quantity of washing soda from a solution of caustic soda (NaOH)? What reactions occur when you add the following substances to washing soda dissolved in water: (*a*) hydrogen acetate, (*b*) slaked lime?

22. Describe clearly two experiments which illustrate the use made in the laboratory of the physical properties of substances (*a*) for identifying substances, (*b*) for preparing substances in a pure state.

23. The gas produced by burning 0.48 gram of sulphur in a large excess of oxygen was passed first over finely divided platinum at a red heat, and then into 100 grams of a 3 per cent. solution of sodium carbonate in water. Give equations representing the changes which occurred in the above experiment, and calculate what weight of solid was left when the resulting liquid was evaporated to dryness and the residue heated strongly. [Na=23, S=32.]

24. From what sources and in what manner is acetic acid prepared? How would you proceed in order to show that acetic acid contains carbon and hydrogen but no nitrogen?

25. Illustrate the meaning of the terms "oxidise" and "reduce" by describing one experiment with hydrogen sulphide and one with some other substance. Give full details of each experiment and draw the apparatus you would use.

26. Describe and explain what takes place when (*a*) nitrate of ammonium, (*b*) nitrate of lead is heated. State how you would collect a specimen of one of the gases produced free from any considerable amount of air.

27. Explain the meaning of the terms "atom" and "molecule," and show that Avogadro's hypothesis gives us a means of determining the relative masses of gaseous molecules.

28. Calculate what weight and what volume, measured at 0° C. and 760 mm. pressure of hydrogen sulphide you could obtain from 5.6 grams of ferrous sulphide. What weight of ferrous sulphide would you take if you were required to collect 200 c.c. of the gas free from air in a measuring cylinder over warm water? Draw the apparatus you would use, and state approximately what would be suitable dimensions for its separate parts.

29. Describe carefully what you see when a current of electricity is passed through a saturated aqueous solution of (*a*) hydrogen chloride, (*b*) sodium chloride. Draw and describe the apparatus you would use in performing these experiments. State briefly what change or changes occur in each case, and say what substances would be left in solution at the end of each experiment.

30. What is silica? How is it found in nature? Describe its appearance and mention its chief chemical properties. State how you would prepare a small specimen of pure silica from a piece of glass.

31. How would you prepare in the laboratory a specimen of phosphoric oxide? Give its properties, and say how you would proceed in order to obtain a few crystals of disodium hydrogen phosphate, $Na_2HPO_4.12H_2O$, from phosphoric oxide.

32. Write a clear and full account of an experiment which shows that sugar yields both alcohol and carbon dioxide when it is fermented by yeast. Draw the apparatus you would use in carrying out the experiment, and state how you would identify these two products.

33. What is the equivalent of an element? 363 c.c. of hydrogen measured at 15° C. and 756 mm. were liberated from a dilute solution of sulphuric acid by 1 gram of zinc; .973 gram of copper was deposited by the action of a solution of copper sulphate on 1 gram of zinc; 1 litre of hydrogen measured at 0° C. and 760 mm. was found to weigh 0.09 gram; from these data calculate the equivalents of zinc and copper.

34. How would you determine experimentally what volume of gas is obtained by heating 1 gram of potassium chlorate? If the barometric pressure were 740 mm. and the temperature were 12° C., what volume of gas ought you to obtain?

35. You are provided with a supply of ammonium nitrate; describe the experiments you would make in order to prepare as many substances as possible from it.

36. Starting from sugar, how would you obtain in the laboratory a specimen of nearly pure alcohol, and from this alcohol how would you obtain acetic acid?

37. If an unknown element were given to you, and you were asked to find out whether it should be classified as a metal or a non-metal, how would you proceed?

38. How can charcoal be converted into graphite and into diamond? What experiments would you make in order to show that the three substances contain only the same element?

39. What reasons can be given for the statement, "sulphur is an element"?

40. What elements are present in (*a*) steel, (*b*) bone, (*c*) china, (*d*) wood, (*e*) a sixpence, (*f*) a sovereign, (*g*) a diamond?

41. Manganese chloride is found on analysis to contain

Manganese	. .	43.63 per cent.
Chlorine	. .	56.36 ,,
		99.99

Calculate its simplest formula. [Mn=55.0, Cl=35.5.]

42. Considering the familiar equation, $2H_2+O_2=2H_2O$, state everything which is conveyed by it.

43. How could you obtain qualitatively—(*a*) Carbon from marsh gas; (*b*) sulphur from hydrogen sulphide; (*c*) chlorine from salt? Describe each process accurately.

44. Explain what is meant by the expression *reducing agent*. Describe two experiments showing that sulphuretted hydrogen is a reducing agent.

45. What is the chemical difference between hard and soft water? How is hard water softened?

46. Wet iron filings are confined with air in a glass tube. Describe all that may be learnt from this experiment.

47. What is an alloy? Mention the names of some common alloys and indicate their qualitative composition.

48. Red oxide of mercury is heated (*a*) alone, (*b*) with carbon, (*c*) with hydrogen. What products are formed, and what weight of each would be obtained, if 10 grams of mercuric oxide were used? [Hg=200, C=12.]

49. Describe any experiments *you have seen* in illustration of the oxidising action of nitric acid.

50. What are the constituents of coal? Describe what happens when coal is burnt in an ordinary open grate.

51. What experiments would you make with sugar to prove that it contains carbon, and with water to prove that it contains oxygen?

52. Describe experiments from which you might infer that the gas which is given off on heating potassium chlorate is identical with one of the constituents of the atmosphere.

53. How may quicklime be employed to detect the presence of two of the four most important constituents of ordinary atmospheric air, and metallic iron to prove the presence of the remaining two? Describe fully the actual experiments you would make.

54. Why cannot hydrogen chloride be made by heating salt with nitric acid? Give the name of one gaseous product which would be formed if the latter acid were inadvertently employed. How is hydrogen chloride usually made and collected? What names are given to its solution in water?

55. What would be the simplest method of making in the laboratory a small quantity of salt starting with metallic sodium ? State carefully how you would carry out the experiment, mentioning any precautions you think it would be advisable to take.

56. How would you prepare and collect a quantity of ammonia gas ? What would be the effect of passing ammonia gas into a dilute solution of nitric acid and then evaporating the solution to dryness and heating the solid residue ?

57. How would you show—(*a*) that water is formed when dry hydrogen chloride is passed over dry lead oxide ; (*b*) that carbon dioxide is formed when alcohol is burned in a spirit-lamp ; (*c*) that oxygen is liberated when lead nitrate is heated ? Draw the apparatus you would use in each experiment.

58. Given a sample of hard water. How would you prepare from it —(*a*) chalk ; (*b*) lime ; (*c*) calcium sulphate ? How would you show that each was free from the other ?

59. Describe the action of heat upon saltpetre, and compare it with what occurs when a small quantity of ammonium nitrate is strongly heated in a test-tube of hard glass. Starting with ammonium nitrate, how would you prepare—(*a*) ammonia ; (*b*) nitrogen ?

60. Explain what you understand by combustion. Describe in detail two different experiments in which combustion proceeds, but in which neither air nor oxygen take any part. Explain how you would proceed in order to regain one of the reacting substances from the product which was obtained in one of the experiments described ?

Answers to Questions

(10) 231 c.c. (11) 141 c.c. (12) 25.4 litres. (13) 13.2 grams. (14) 4.69 litres. (15) 27.2 (16) 33.9. (17) 31.2.

(18) H = 2.04% N = 82.4% C = 40.00% Na = 27.4% C = 42.1%
S = 32.65% H = 17.6% H = 6.66% H = 1.2% H = 6.4%
O = 65.30% O = 53.33% C = 14.3% O = 51.4%
O = 57.1%

(19) $(C_3H_7O_3)x$, where x is a small whole number. (20) C_2H_6O. (21) 135. (22) 208. (23) 95. (24) 15.84. (25) 207. (27) 653 c.c. (28) 7 molecules. (30) 32 grams. (31) .0925 gram per c.c. (32) 8.2% impurity. (58) (*a*) 234 c.c., (*b*) 599.5 c.c., (*c*) 24.1 c.c., (*d*) 85.2 c.c. (59) 64.2 c.c. (60) Tube B. (66) 40.3. (67) 15.3 (68) 32.1. (69) 28 and 18.66. (70) Equiv. = 35. Sulphuric acid = .49 gram. (71) 30.5. (72) 36.1. (73) 127. (74) 4.96 grams. (75) 4.78 grams. (76) 55.8 grams. (77) 498 c.c.

(78) (*a*) Cu = 39.62 (*b*) Zn = 22.65 (*c*) N = 26.2 (*d*) Ag = 63.6 (*e*) Al = 3.06
S = 20.12 S = 11.15 H = 7.4 N = 8.2 P = 31.62
O = 40.25 O = 61.31 Cl = 66.3 O = 28.2 O = 65.31
H = 4.88

(79) C_5H_7N. (80) $C_7H_6O_2$. (81) $C_3H_5N_3O_9$. (82) $CoI_2.4H_2O$. (83) 84.6. (84) 209.8. (85) 130.66. (86) .928° C. (87) 27.6. (88) 74.97.

(89) (*a*) 40, (*b*) 120, (*c*) .0533. (90) 40.58. (91) .00816 gram per c.c. (92) 190.5 c.c. (93) 18 c.c. (94) .0169 gram of $BaCl_2$ per c.c. (95) 9.09. (96) 28.57 (97) 72.5. (98) .7 gram. (99) .238 gram ferrous iron, .311 gram ferric iron. (100) 6.12 grams.

Answers to Numerical Examples in Matriculation Questions.

(1) 178.5 litres. (7) 31.8.

(11) 450 c.c.

(18) 29.2 grams per litre. (23) 3.54 grams, consisting of 1.41 grams of Na_2CO_3 and 2.13 grams of Na_2SO_4.

(28) 2.163 grams of H_2S; 1.415 litres of H_2S.

(33) Zinc = 32.4; copper = 31.5. (34) 292 c.c. (41) $MnCl_2$. (48) (*a*) Mercury, 9.26 grams; oxygen, .74 gram. (*b*) Mercury, 9.26 grams; carbon monoxide, 1.29 grams. (*c*) Mercury, 9.26 grams; water, .83 gram.

(63) 74.7 grams. (68) 66.6% nitrogen : 33.3% oxygen. (76) Weight of a litre = 1.44 grams; density 16.

(84) NH_4NO_3; N_2O. (90) 53.1 c.c.

(92) 7. (98) .717 gram oxygen; 9.283 grams metal; equivalent weight 103.5.

(100) (*a*) 56° for potassium nitrate and 34° for sodium nitrate. (*b*) 68°; 20 grams more of potassium nitrate than of sodium nitrate separate.

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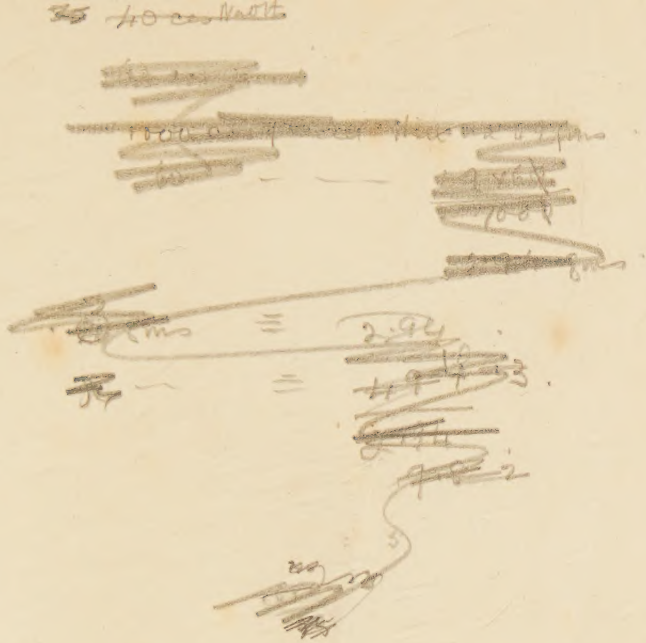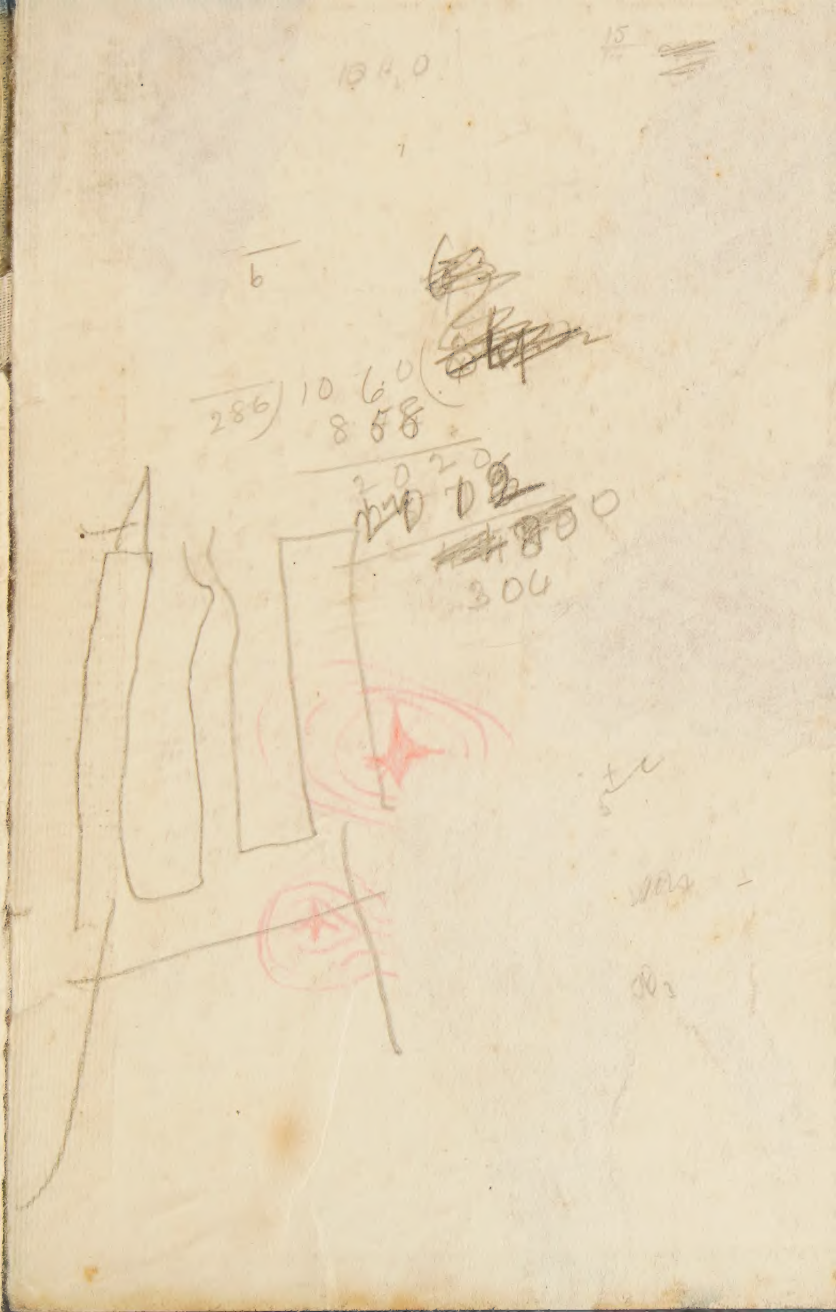
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